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THE LUMINESCENCE OF DIAMOND AND ITS RELATION TO CRYSTAL STRUCTURE

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Received August 14, 1950

1. Introduction

Studies on the luminescence exhibited by diamond under ultra-violet irradiation were commenced at Bangalore some ten years ago. Their scope enlarged as the collection of high-grade material available for the investigations grew and became more fully representative in character. The results of the researches of the first few years were reviewed in two papers[1, 2] published together in these *Proceedings* in the year 1944. The conclusions reached in those papers may be stated briefly as follows:—

I. *Nearly all diamonds and especially those of the first quality exhibit luminescence: this effect is an inherent property of the material: the variations observed in its intensity and in its spectral character have a structural origin.*

II. *The symmetry of the electronic structure of diamond may be either tetrahedral or octahedral: in individual specimens there is a commingling of the different possible structures having these types of symmetry and the property of luminescence results therefrom.*

Experimental evidence was presented both at that time[3] and also later[4, 5] that variations of behaviour having a structural origin present themselves not only in respect of luminescence, but also in respect of numerous other physical properties of diamond, *viz.*, the intensity and angular divergence of the X-ray reflections by the crystal, its infra-red absorption spectrum of the first-order, the absorption spectra in the remote and near ultra-violet and in the visible region, structural birefringence and photo-conductivity. The variations observed in all these properties are manifestly correlated with each other, thereby demonstrating their common physical origin.

The structural origin of the luminescence of diamond can be very elegantly exhibited with the aid of polished cleavage plates of the crystal and by various methods of observation. One of these is an examination of the behaviour of such plates in respect of luminescence under ultra-violet irradiation and in respect of birefringence in ordinary light. A remarkable parallelism between these two phenomena was discovered by one of us.[6]

Photographs were published in these *Proceedings*[7] which were intended to exhibit them side by side for purposes of comparison. Unfortunately, however, the techniques employed were defective, and the pictures reproduced convey only a feeble idea of the very remarkable and precise character of the relationship between luminescence and birefringence in diamond. The present paper is intended to remedy this defect in the earlier work. The photographs now published in the Plates accompanying the paper are a record of the luminescence and birefringence of some of our typical specimens. The photographs are on precisely the same scale and have the same orientation, thus enabling them to be readily compared with each other. There are over a hundred cleavage plates of diamond of the first quality in our collection, and the summary of the facts noticed in the case of the diamonds whose photographs are reproduced is equally a description of the behaviour of the rest of them.

2. Technique of Study

The spectral character of the luminescence of diamond has been thoroughly investigated by P. G. N. Nayar[8] and by Anna Mani[9] at Bangalore. On cooling the diamond down to low temperatures, it becomes evident that the luminescence has its origin in various electronic transitions in the crystal, either alone or in combination with its vibrational transitions. Comparison of the spectra of numerous specimens shows that the emission is of two distinct kinds, a *blue luminescence* and a *greenish-yellow luminescence* respectively. Their absolute and the relative intensities vary largely. The blue luminescence arises principally from an electronic transition giving a line at 4152 A.U. near the violet end of the spectrum, accompanied by a vibrational spectrum appearing in the blue and green regions. The greenish-yellow luminescence arises *principally* from an electronic transition giving a greenish-blue line at 5032 A.U. accompanied by a vibrational spectrum appearing in the green and yellow regions. The two types of luminescence may be viewed separately by observing the diamond through appropriately chosen colour filters. A piece of cobalt glass transmits only the blue luminescence and cuts off the other. For isolating the greenish-yellow luminescence, we have found that an orange-yellow filter which has a complete cut-off at 5400 A.U. is preferable to an yellow filter with a cut-off at about 5000 A.U., since the blue luminescence has a sensible intensity in the region between 5000 and 5400 A.U.

Sunlight concentrated by a large lens and passed through a nickel-oxide glass filter furnishes ultra-violet illumination of the requisite intensity to excite the luminescence. It is focussed on the diamond which is placed on

a plate of black glass, both being carefully cleaned to minimise scattered light. It is arranged that the ultra-violet irradiation is almost tangential to the surface of the specimen and as nearly uniform over it as possible, while the visible luminescence is viewed nearly normally to the surface. In this way, the trouble due to reflection and scattering of the red light simultaneously transmitted by the ultra-violet filter is minimised. In some cases, entry of light through the facetted edges of the diamond results in a streaky illumination of its interior. This trouble is avoided or minimised by a proper choice of the setting of the diamond in its own plane. The camera with which the specimen is photographed is a vertical one of rigid construction and of fixed focal length. It is fitted with a high-quality short-focus lens of the type used for making enlarged photographic prints from small negatives. The appropriate colour filter is interposed between the camera and the diamond. When the cobalt-blue glass is used as a filter, a cell containing sodium nitrite solution has to be interposed to prevent scattered and reflected ultra-violet radiation from entering the camera.

The birefringence is recorded with the same camera and under the same conditions as the luminescence, except that the illumination is by ordinary light transmitted normally through the diamond held between crossed polaroids, no filters being used. The photographs of luminescence and birefringence are thus on exactly the same scale and therefore strictly comparable. The record of the birefringence is to some extent influenced by the setting of the specimen in its own plane between the crossed polaroids. This is varied until the features which it is desired to exhibit are most clearly visible.

3. The Facts of Observation

Each of the Figs. 1 to 14 appearing in Plates VI to XII contains three photographs marked (*a*), (*b*), (*c*); these represent respectively the blue luminescence, the greenish-yellow luminescence and the birefringence of the diamond. They are placed together for ease of comparison. We shall not comment on the figures individually, but proceed to state the facts emerging on a careful study made with the specimens in our collection. The interested reader can readily verify these statements by an examination of the figures reproduced.

A. A few diamonds are non-birefringent. Such diamonds exhibit only blue luminescence, the greenish-yellow type being absent.*

* During a visit by one of us to Great Britain in May 1948, the opportunity arose of examining the luminescence of a great number of diamonds of the highest grade in their natural form as crystals. These had been sorted and arranged in cages in the order of their

B. A few diamonds show neither the blue nor the greenish-yellow luminescence. Such diamonds exhibit a characteristic type of birefringence consisting of a set of fine streaks parallel to each other, or sets of such parallel streaks intersecting each other.

C. The majority of diamonds exhibit both types of luminescence. They also exhibit a birefringence pattern, the geometric character of which bears a recognisable relationship to the features observed in one or the other or both of the luminescence patterns.

D. The two kinds of luminescence often exhibit certain geometric features in common. In other cases, they appear to be complementary, dark regions in one being bright regions in the other, and *vice versa.* Frequently, also, the greenish-yellow luminescence exhibits features totally absent in the blue luminescence.

E. The blue luminescence is usually conspicuous in areas where the birefringence is weak or absent. It often exhibits a remarkably uniform intensity over such areas. On the other hand, in areas where there is strong birefringence, the blue luminescence is generally of non-uniform intensity and may exhibit a banding which is often straight, but may sometimes also be wavy.

F. The greenish-yellow luminescence frequently takes the form of sets of bands running parallel to each other. Sometimes, two or even three such sets of bands may be seen. Corresponding sets of bands are visible in birefringence.

G. The greenish-yellow luminescence is often conspicuous in the regions separating areas in which birefringence is weak or absent from those which exhibit a strong birefringence.

H. One can distinguish the character of the birefringence in the areas which display both blue and greenish-yellow luminescence or the latter alone, from the birefringence in the areas which display neither. The areas of the latter kind exhibit birefringence of the same character as the non-luminescent diamonds.

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excellence, as judged by their water, freedom from colour and the absence of strong birefringence when examined between crossed polaroids. Each cage contained some fifty or sixty crystals. All the diamonds without exception from the first six cages showed luminescence of blue colour. Examples of green or yellow luminescence were very few even in the cages containing the lower grades. A blue or bluish-green luminescence was by far the commonest. The batch of diamonds studied was from the Congo, and the similarity between these results and those observed with Indian diamonds of high grade during a visit to Panna in June 1942 was very striking.

Figs. 15 and 16 in Plate XIII illustrate an effect observed with all diamonds which exhibit the greenish-yellow luminescence as a set of parallel bands. Inclining the plate about an axis parallel to the bands, it is found that the bands sharpen to fine lines when the plate is tilted to one side, while they become more diffuse when the tilt is on the opposite side. In the same circumstances, the bands in birefringence sharpen to fine lines or become more diffuse respectively, thus displaying a complete parallelism of behaviour with the bands in luminescence. Figs. 15 (*b*) and (*c*) exhibit these effects with a tilt to one side, and Figs. 16 (*b*) and (*c*) with the tilt on the other.

In this connection, a reference should be made to the facts elicited concerning the birefringence of polished cleavage plates of diamond in the very thorough study by G. N. Ramachandran.[10] This author made use of a Zeiss petrographic microscope with a Federov universal stage on which the diamond could be placed and suitably orientated. He examined many plates apparently different in their behaviour, and the investigation showed that in all cases, the birefringence patterns were resolved by the microscope with a suitable tilt of the plate to a set of laminations having a definite orientation parallel to either the octahedral or the dodecahedral planes in the crystal. This was found to be the case even when no laminations were visible when the plate was viewed *normally* between crossed nicols. Only in the diamonds which exhibited no visible birefringence were such laminations found to be absent. In other words, birefringence when observed in diamond is associated with a laminated structure in the crystal: the laminæ run parallel to the octahedral or to the dodecahedral planes in the space-lattice.

4. The Origin of the Luminescence

The view formerly held regarding the luminescence of diamond was that it did not represent a characteristic property of that substance and that the emission was due to some undetermined impurity present in it; the impurities suggested from time to time made a long list, *viz.*, samarium, yttrium, sodium, aluminium, chromium, iron, and titanium, and included even some hydrocarbons! However, it became clear from even the earliest Bangalore investigations that this view was irreconcilable with the observed spectral characters of the luminescence and of the associated absorption. Nayar in his papers of 1941 recognized that the spectroscopic evidence showed the luminescence to be a characteristic property of diamond itself. He ventured further to suggest that the variations of its intensity were in some way connected with the question of the structural perfection of the crystal. A more extensive collection of material became available soon afterwards, and other methods of investigation were also applied to the

problem. These enabled more definite conclusions to be reached and published, as already mentioned in the introduction.

It is clearly not possible to reconcile the view which regards the luminescence of diamond as an emission by some undetermined impurity with the experimental facts which we know to-day about the subject. It is not possible, either, to entertain the alternative but scarcely less naive hypothesis put forward by some authors, namely that the luminescence is that of diamond *activated* by a trace of some unknown impurity. Indeed, it is obvious that no activator, however distributed within the crystal, could account for the curious and remarkable relationships between luminescence and birefringence observed to exist, as set out in the foregoing pages. Nor would it be capable of accounting for the quantitative relationships which exist between luminescence intensity and X-ray reflection phenomena in diamond as demonstrated by G. N. Ramachandran[11, 12, 13] by three different methods. These relationships form a direct and convincing demonstration that luminescence in diamond has a structural origin. In these circumstances, it seems almost superfluous to refer to many other facts which have been fully established for which it would scarcely be possible to offer any reasonable explanation on the "activator" hypothesis. We shall content ourself here with mentioning the very striking results obtained by K. G. Ramanathan,[14] who has shown that the luminescence intensity and the infra-red absorption by diamond stand in the closest relation with each other.

5. Luminescence and Crystal Structure

The clue to an understanding of the luminescence properties of diamond is to be found in a consideration of the symmetry properties of the structure of that crystal.* The leading crystallographers of the nineteenth century, including especially Groth, came to the conclusion that the crystal symmetry of diamond was of the tetrahedral class, and that the octahedral symmetry frequently exhibited by it was a pseudo-symmetry arising from an interpenetration of the positive and negative tetrahedral forms. Fersmann and Goldschmidt made a thorough study of the subject[15] and arrived at the same conclusions. The crystal forms of diamond have been re-examined from a completely new point of view,[16] and the results support the earlier findings with one modification, namely that the possibility of the structure of diamond being octahedral in some cases is not excluded. The position thus reached

* In the article on Diamond in Volume 3 (p. 69–89) of the Encyclopedia of Chemical Technology (Edited by Professors Kirk and Othmer of the Brooklyn Polytechnic Institute, and issued by the Interscience Publishers, 1949), it is shown how this also enables the remarkable variations in physical properties exhibited by diamond to be correlated and interpreted in a coherent and intelligible manner.

is that there are alternative possibilities, in other words that the symmetry of the structure may be either tetrahedral or octahedral.

The existence of structures belonging to the two different symmetry classes would at once explain why the strength of the infra-red absorption of the first order in diamond is highly variable. Spectroscopic theory permits us to identify the structures which are infra-red active with those possessing tetrahedral symmetry and those which are inactive as possessing octahedral symmetry. We can also understand without difficulty why some diamonds which are infra-red active are optically isotropic. The positive and negative tetrahedral forms are physically identical and only geometrically different. Hence their interpenetration would not lead to birefringence. On the other hand, the lamellar structure of the infra-red inactive diamonds indicates that there are also two sub-types of octahedral structure: but these are physically different and therefore do not interpenetrate but appear in distinct layers, the octahedral or dodecahedral planes of the lattice being the planes of junction, analogous to be the composition planes in polysynthetic twinning. Such a juxtaposition naturally results in birefringence.

Viewed against the theoretical background sketched above, the facts stated in the preceding sections naturally fall into place. Tetrahedral and octahedral symmetry do not give us different kinds of diamond but only different kinds of structure. If the positive and negative tetrahedral structures co-exist, interpenetrating each other, we have non-birefringent blue luminescent diamond. If the two sub-types of octahedral symmetry co-exist, we have birefringent non-luminescent diamond. In the great majority of cases, however, the tetrahedral and octahedral structures co-exist with the result that the diamond is birefringent and exhibits both blue and greenish-yellow luminescence. The latter arises at the junction planes between the tetrahedral and octahedral structures, and it is readily understood, therefore, why it exhibits a banded structure.

Similar considerations enable us to understand the variations in the behaviour of diamond in respect of infra-red activity, as also in respect of their ultra-violet absorption. In sufficiently thin layers,[17] *all* diamonds exhibit ultra-violet transmission up to 2250 A.U., there being an intense absorption at still shorter wave-lengths. A weaker absorption at longer wave-lengths is characteristic of the electronic structures having tetrahedral symmetry. Hence, the strength of such absorption varies from diamond to diamond in a manner closely correlated with their behaviour in respect of luminescence. If the diamond is completely non-luminescent, the cut-off appears at 2250 A.U. even with thick plates. On the other hand, if the

diamond is of the luminescent kind, the thicker plates exhibit absorption at wave-lengths greater than 2250 A.U., and in the case of the feebly blue-luminescent non-birefringent diamonds this extends up to about 3000 A.U.

6. Some Remarks on Nomenclature

References continue to appear in the literature which assume that any actual diamond must belong to either the one or the other of two species designated as Type I and Type II respectively. This assumption does not correspond with reality. The original proposers of that nomenclature noted that the great majority of diamonds showed optical birefringence and also infra-red activity in the 8 μ region of the spectrum. They assumed that such optical anisotropy and infra-red activity were characteristic of a particular type of diamond including the great majority of specimens which they designated as Type I. On the other hand, they found that a small minority of diamonds were inactive in infra-red absorption in the 8 μ region and exhibited a lamellar structure. These diamonds, they designated as belonging to Type II. Actually as we have seen, diamonds are forthcoming which show the infra-red activity strongly but do not show any visible birefringence. Moreover, examination on the Federov stage with a polarising microscope shows that all diamonds which show birefringence also exhibit a lamellar structure. Further, the infra-red activity of diamond in the 8μ region is variable and may be anything from zero upwards. Hence it is not possible to divide diamond into two classes on the basis of the presence or absence of such activity. Neither is it possible to base such a classification on the degree of transparency of diamond in the ultra-violet region of the spectrum between 2250 A.U. and 3000 A.U., since this varies in a continuous manner from diamond to diamond.

It is thus clear that the classification of diamond as belonging to Type I or Type II was based on erroneous beliefs concerning the actual facts of the case. A proper scientific classification must be based on a definite physical idea of what the structural differences actually observed represent and should be capable of correctly describing and interpreting the observed facts. Since this is not the case for the division of diamond into two types and since such division does not correspond with reality, it is meaningless and quite misleading and should therefore be discarded. The truth of the matter is that the great majority of diamonds have a structure which does not permit of their being labelled as belonging to any single type.

Acknowledgement

We take this opportunity of acknowledging the generous assistance which was forthcoming when one of us visited London in May 1948, facilities

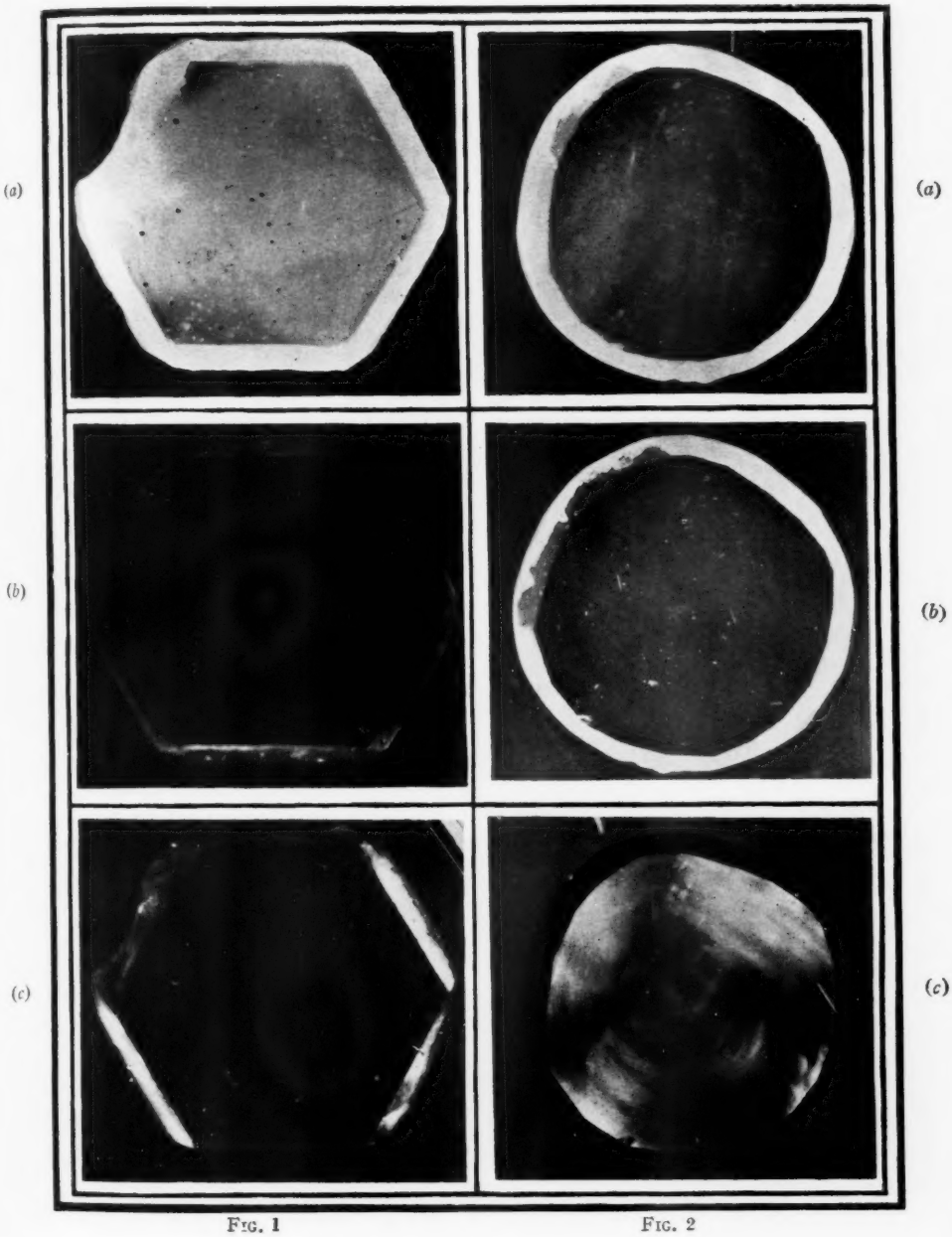


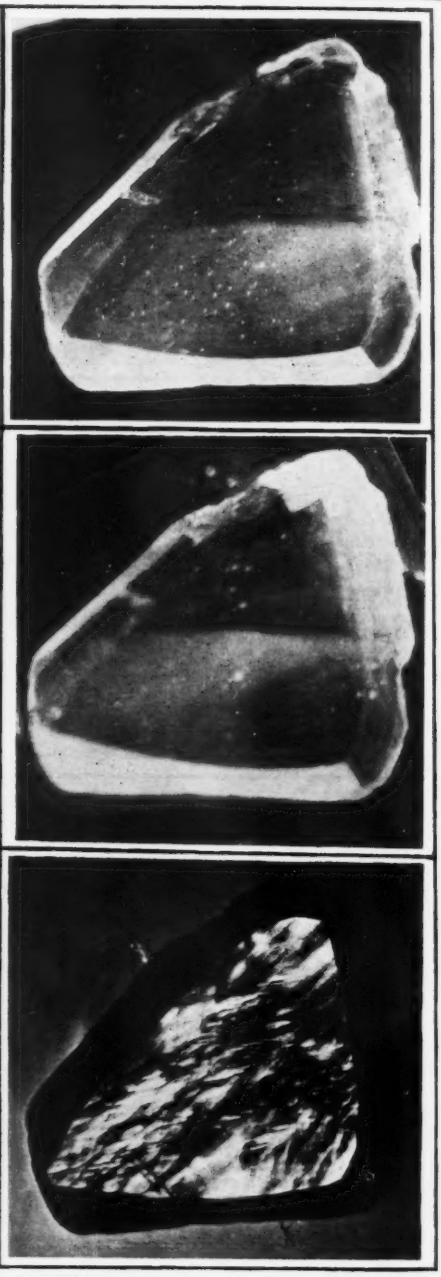
FIG. 1 FIG. 2

(*a*)

(*b*)

(*c*)

FIG. 3



(*a*)

(*b*)

(*c*)

FIG. 4

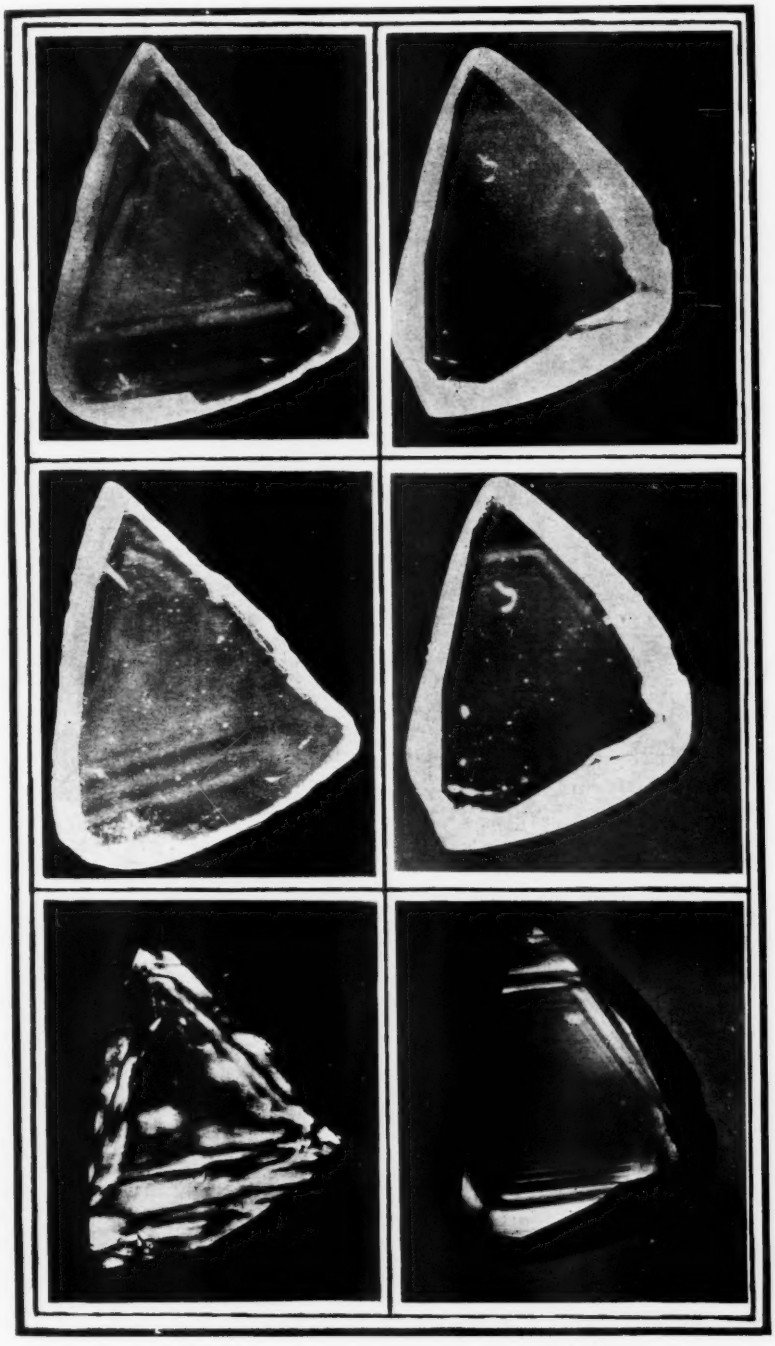
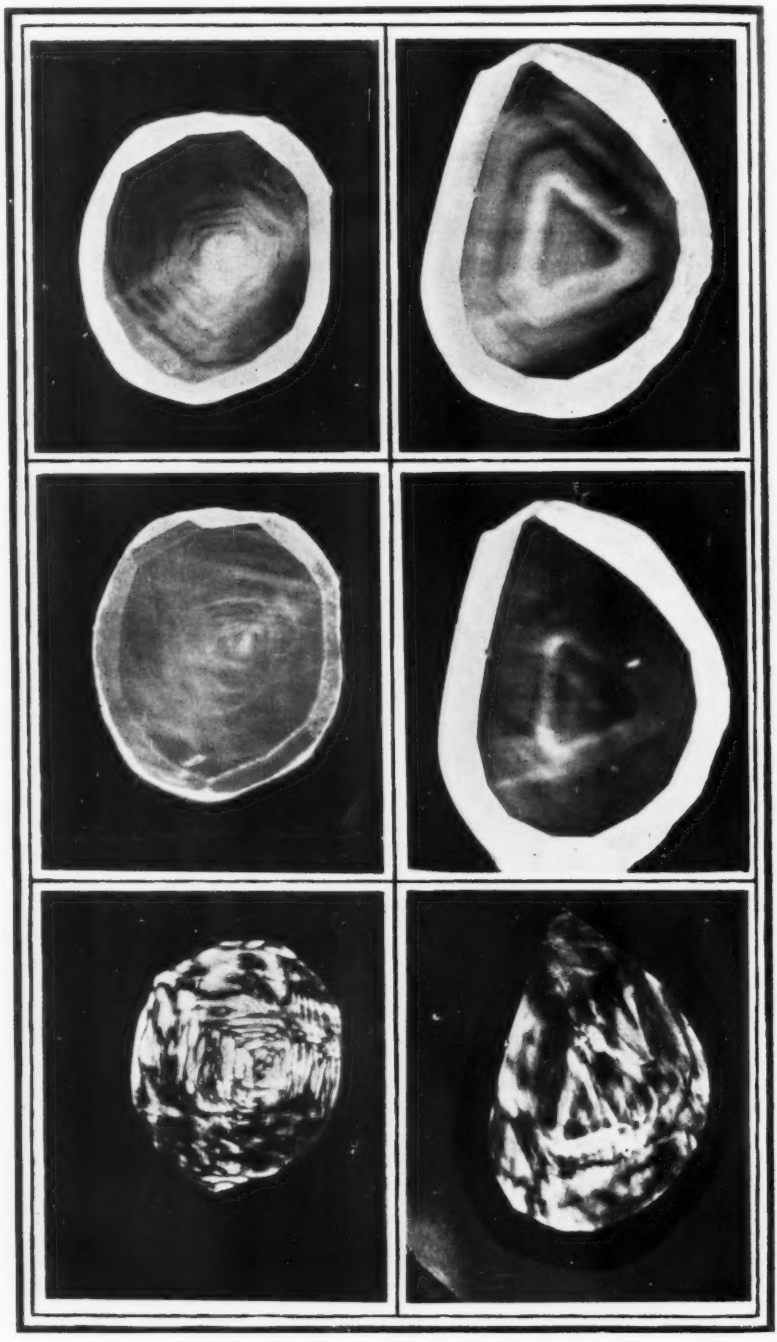


FIG. 5 FIG. 6

(*a*)

(*b*)

(*c*)



(*a*)

(*b*)

(*c*)

FIG. 7 FIG. 8

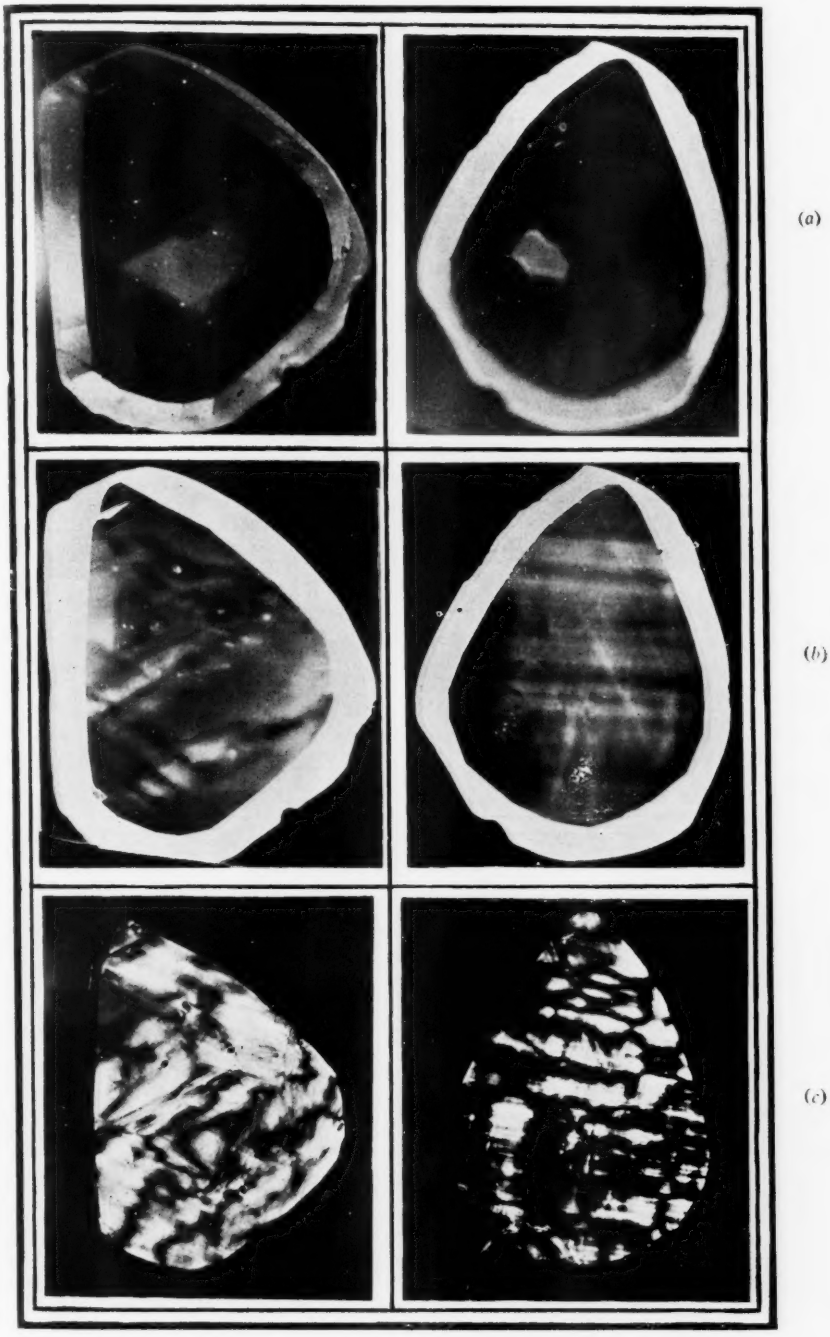


FIG. 9 FIG. 10

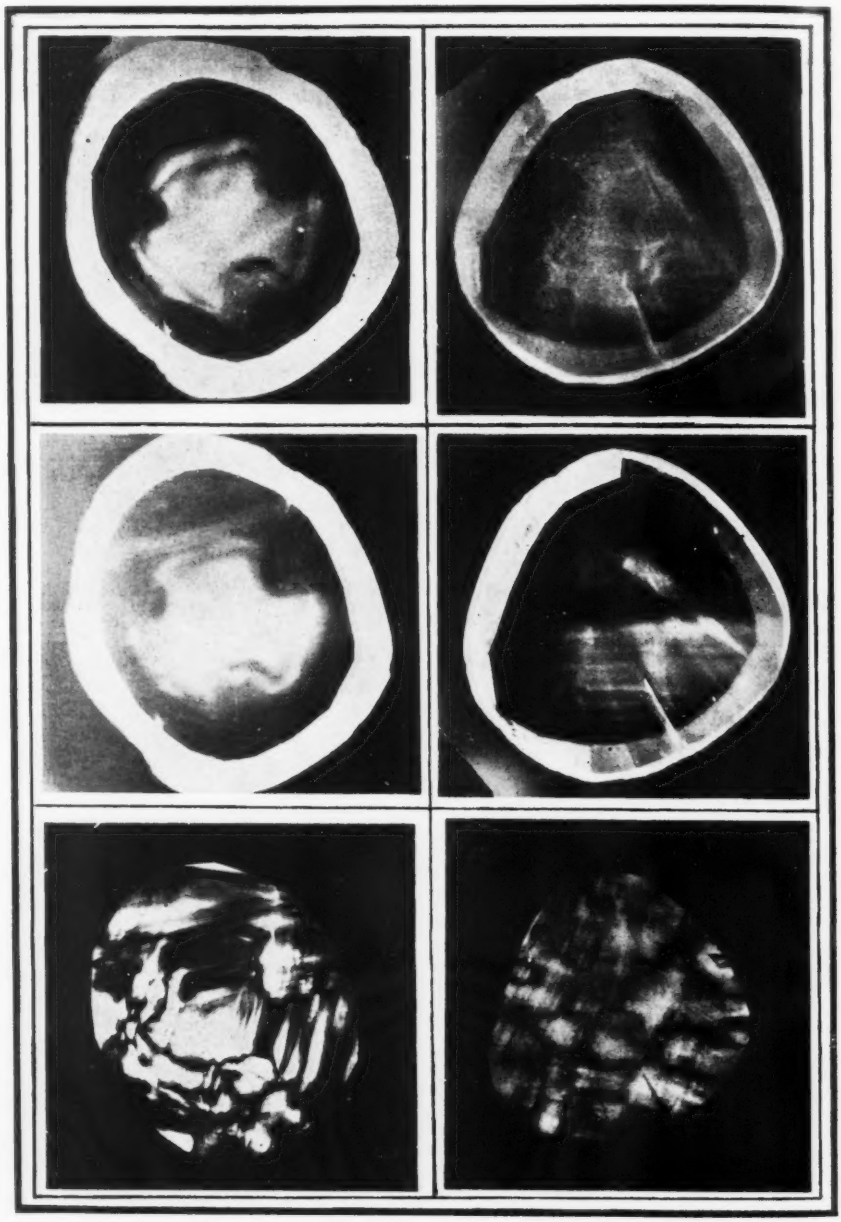


FIG. 11 FIG. 12

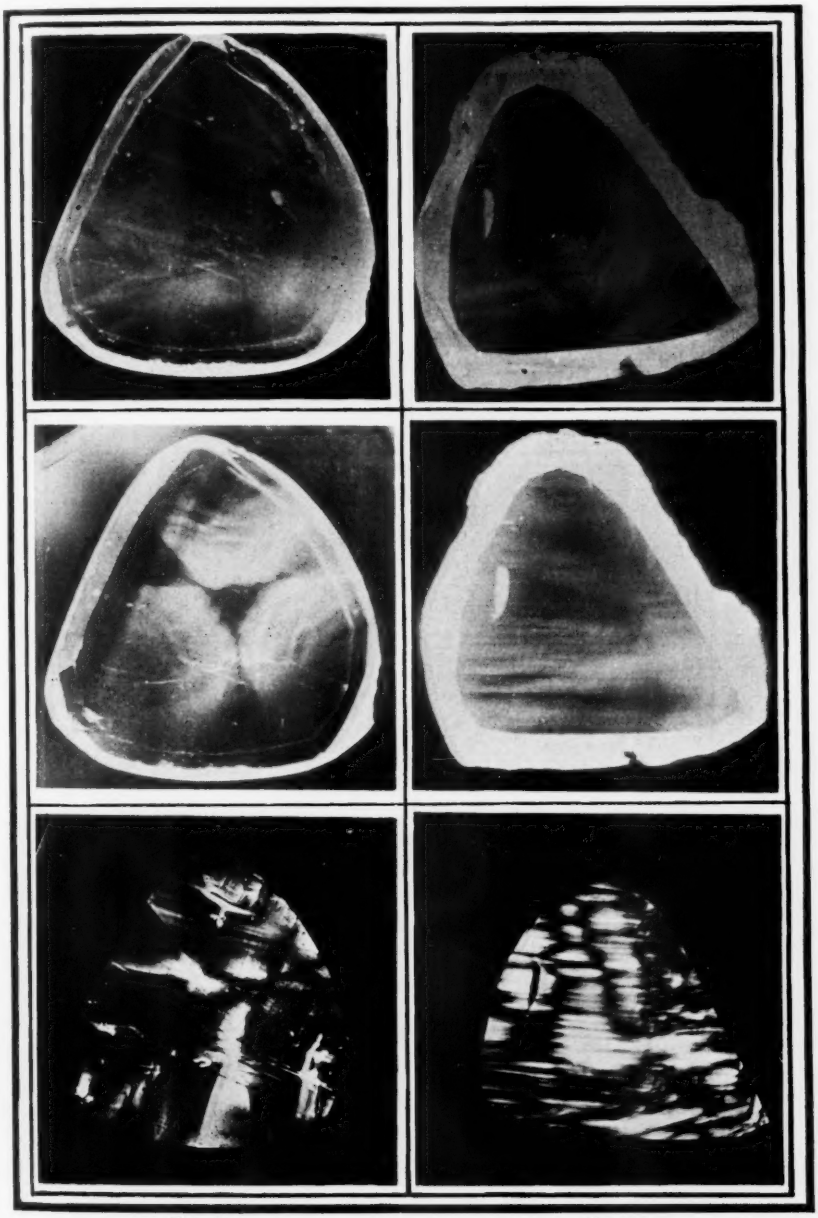
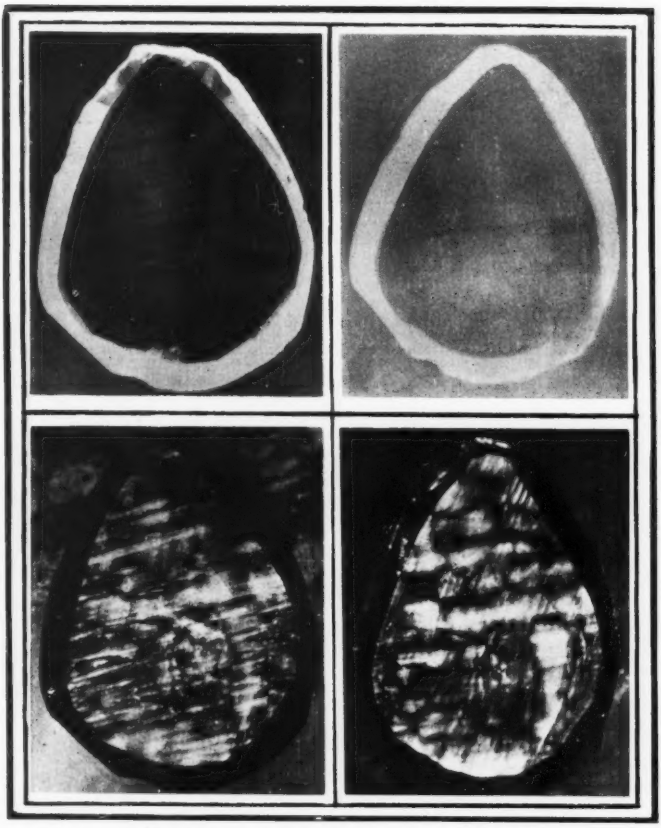


FIG. 13 FIG. 14

(*b*)

(*c*)



(*b*)

(*c*)

FIG. 15

FIG. 16

for study and specimens for further investigations having been freely placed at his disposal by several persons and authorities. We wish to mention and specially offer our thanks to Dr. Paul Grodzinski and to Mr. B. W. Anderson. The diamond of which the photographs are reproduced as Fig. 1 was one of the specimens received as a gift during the visit. To the Instruments and Chemicals Ltd. of Ambala, we are also much indebted for the prompt construction of the stand-camera used in obtaining the photographs and for their generosity in making a gift of it to this Institute.

Summary

The relationships which exist between the luminescence of diamond and its behaviour in respect of birefringence are described and illustrated in the paper by a new series of photographs obtained with improved technique and with diamonds of the first quality. It is shown that the results fully support the conclusions reached earlier, *viz.*, that the luminescence of diamond has a structural origin. It is also pointed out that the classification of diamond into two species as Type I and Type II does not correspond with reality and must therefore be discarded.

References

1. C. V. Raman .. *Proc. Ind. Acad. Sci.*, A, 1944, **19**, 189.
2. ———— .. *Ibid.*, 1944, **19**, 199.
3. "First Symposium on Diamond," .. *Ibid.*, June issue, 1944, **V. 19.**
4. "Second Symposium on Diamond," .. *Ibid.*, July issue, 1946, **V. 24.**
5. "Symposium on the Vibration Spectra of Crystals," .. *Ibid.*, December issue, 1947, **V. 26.**
6. C. V. Raman .. *Current Science*, 1943, **12**, 33.
7. G. R. Rendall .. *Proc. Ind. Acad. Sci.* **A**, 1946, **24**, 168.
8. P. G. N. Nayar .. *Ibid.*, 1941, **13**, 483.
   ———— .. *Ibid.*, 1941, **13**, 534.
   ———— .. *Ibid.*, 1941, **14**, 1.
   ———— .. *Ibid.*, 1942, **15**, 293.
9. (Miss) Anna Mani .. *Ibid.*, 1944, **19**, 231.
10. G. N. Ramachandran .. *Ibid.*, 1946, **24**, 65.
11. ———— .. *Ibid.*, 1944, **19**, 280.
12. ———— .. *Ibid.*, 1944, **19**, 304.
13. ———— .. *Ibid.*, 1946, **24**, 95.
14. ———— .. *Ibid.*, 1947, **26**, 469.
15. Fersmann and Goldschmidt .. *Der Diamant, C. Winter, Heidelberg*, 1911.
16. C. V. Raman and S. Ramaseshan .. "Second Symposium on Diamond," *Proc. Ind. Acad. Sci.*, A, 1946, **24**, 1.
17. K. G. Ramanathan .. *Ibid.*, 1946, **24**, 137.

THE TIME OF SETTING OF GELS FORMED BY THE MUTUAL INTERACTION OF OPPOSITELY CHARGED SOLS AT DIFFERENT TEMPERATURES

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Recently Prasad and Mehta[1, 2] have shown for the first time that gelation takes place when certain well-defined volumes of some oppositely charged sols of suitable concentrations, dialysed or undialysed, are mixed together in suitable proportions. They have also measured the time of setting (t) of such gels which follows the relation $t = Ra^{-m}$, where 'a' is the volume of one of the oppositely charged sols added to 5 c.c. of the other, and R and m are constants.

The present authors have established that gels are obtained by mixing (i) the positively charged aluminium hydroxide sol with negatively charged sols of antimony sulphide, silicic acid and manganese dioxide, and (ii) the negatively charged nickel hydroxide sol, dialysed to different extent, with the positively charged sol of silicic acid and undialysed and dialysed sol of ferric hydroxide. They have measured the time of setting of these gels and have examined the effect of temperature on the time of setting which for inorganic gels generally decreases as the temperature is increased.[3]

Experimental

(*a*) *Preparation of gels*: (1) *Aluminium hydroxide sol* (+ *ve*).—It was prepared by Crum's method and was dialysed for 1, 2, 3 and 4 days. Three different samples of the sol (A, B and C) were prepared and the undialysed and dialysed samples were labelled as A, A_1, A_2, A_3 and A_4, B, B_1, B_2, B_3 and B_4 and C, C_1, C_2, C_3 and C_4. One litre of each of the three samples was found to contain aluminium hydroxide corresponding to 2·30 g., 2·33 g., and 2·31 g. of Al_2O_3, respectively. The aluminium hydroxide content of the undialysed and the dialysed samples were found to be practically constant.

(2) *Antimony sulphide sol* (− *ve*).—It was prepared by adding slowly a saturated solution of H_2S to a dilute solution (3 g. in 300 c.c.) of potassium antimony tartrate. The excess of H_2S was driven out by slow boiling and the last traces were removed by bubbling hydrogen gas. The sol was labelled as D. Its colloidal content was found to correspond to 0·72 g. of Sb_2S_3 per litre.

(3) *Manganese dioxide sol* (— *ve*).—It was prepared by the reduction of potassium permanganate with sodium arsenite and its colloidal content was found to correspond to 0·52 g. of MnO_2 per litre. It was labelled as E.

(4) *Silicic acid sol* (+ *ve*).—It was prepared by adding gradually a solution of sodium silicate to a solution of HCl with vigorous stirring. The resultant mixture was dialysed until it was nearly free from chloride ions. The dialysate was replaced with fresh distilled water as frequently as considered necessary. The colloidal content of the sol was found to correspond to 29·74 g. of SiO_2 per litre of the sol. It was labelled as F.

(5) *Silicic acid sol* (— *ve*).—The negatively charged sol was obtained by adding suitable amount of sodium hydroxide solution to the positively charged sol prepared in the manner described above. Its colloidal content was found to correspond to 27·27 g. of SiO_2 per litre. It was labelled as G.

(6) *Nickel hydroxide sol* (— *ve*).—It was prepared by the method of Prasad and Mehta.[4] The samples of the undialysed sol and those of the sol dialysed for 1, 2, 3 and 4 days were labelled as H, H_1, H_2, H_3 and H_4. The colloidal content of the sol corresponded to 3·33 g. of nickel in one litre, and was found to be practically constant in all the five samples.

All sols were stored in Jena glass bottles.

(*b*) *Cataphoretic speed.*—The cataphoretic speeds (V = in cm. per second per volt) of the sols were measured by Mukerjee's apparatus under conditions given below:

E.M.F. applied = 100 volts; distance between the side tubes = 4·2 cm.; potential applied at the boundary = 6·06 volts; current passed for 1,260 seconds in sols A, B, C, D, E and G and for 840 secs. in F and H.

TABLE I

Sol.	V × 10^4	Sol	V × 10^4	Sol.	V × 10^4	Sol.	V × 10^4
A	3·664	B_1	5·269	C_2	5·299	G	1·208
A_1	5·039	B_2	5·955	C_3	6·985	H	7·264
A_2	6·528	B_3	6·916	C_4	8·017	H_1	8·762
A_3	8·017	B_4	7·902	D	9·390	H_2	10·300
A_4	9·990	B_5	3·321	E	2·107	H_3	5·611
B	3·550	C_1	5·153	F	1·218	H_4	4·982

The upper liquid was dilute solutions of HCl (Merck's extra pure) in the case of aluminium hydroxide sol and KCl (Merck's extra pure) for other sols. The conductivities of the solutions were nearly the same as those of the sols but their densities were slightly lower. The colourless sols were coloured by the addition of 0·01 c.c. of 1 per cent. solution of neutral red to 40 c.c. of the sol. The results obtained are given in Table I.

(*c*) *Characters of the gels obtained by mutual gelation.*—The gels obtained by mixing the oppositely charged sols vary in transparency, firmness and colour. The characteristics of these gels have been observed in Table II.

TABLE II

	+ve sol.	−ve sol.	Colour	Transparency	Firmness
1.	Aluminium hydroxide	Antimony sulphide	Orange-yellow	Transparent	Not very firm
2.	,,	Silicic acid	Colourless	Semi-transparent	Quite firm
3.	,,	Manganese dioxide	Dark brown	Semi-transparent	Not very firm
4.	Silicic acid	Nickel hydroxide	Green	Quite transparent	Very firm

(*d*) *Measurement of the time of setting.*—The times of setting were measured at various temperatures, by Hurd and Letteron's method[7] modified by Miss Nathan.[5]

A number of test-tubes were filled with 5·0 c.c. of one sol, marked I. In another set of test-tubes, different known volumes (measured by a micro-pipette reading upto 0·01 c.c.) of the oppositely charged sol, marked II, were taken and diluted to 5·0 c.c. by the addition of distilled water. The test-tubes were well corked and were placed in the thermostat for half an hour. The contents of the two test-tubes were mixed a number of times and well shaken. The mixture was then poured into a small weighing bottle and a stop-watch was started. A glass rod 3″ long and 1 mm. in diameter was introduced in position. When the glass rod could remain in its position without the aid of the mechanical support, the stop-watch was stopped and the time noted. To increase the accuracy of measurements, a number of readings were taken, each time disturbing the gel-forming mixture as few times as possible. The minimum time obtained in this manner was taken as the time of setting of the gel.

The results obtained are given in Tables III–XIV in which (t) with a suffix denotes the time of setting of the gel at the temperature in centigrade indicated by the suffix.

TABLE III

$I(A)(+ve)$, $II(D)(-ve)$

D. in c.c.	t_{35}	t_{40}	t_{45}
1·8	1′–13″	1′–7″	0′–58″
1·9	0′–54″	0′–53″	0′–50″
2·0	0′–42″	0′–40″	0′–38″
2·1	0′–32″	0′–29″	0′–28″
2·2	0′–24″	0′–23″	0′–23″
2·3	0′–20″	0′–17″	0′–16″

TABLE IV

$I(A_1, A_2)(+ve)$, $II(D)(-ve)$

D in c.c.	t_{35}	t_{40}	t_{45}	D in c.c.	t_{35}	t_{40}	t_{45}
2·0	2′–3″	1′–44″	1′–26″	2·5	3′–30″	3′–3″	2′–30″
2·1	1′–29″	1′–16″	1′–1″	2·6	2′–55″	2′–35″	2′–5″
2·2	1′–12″	1′–4″	0′–56″	2·7	2′–32″	2′–12″	1′–53″
2·3	0′–55″	0′–46″	0′–40″	2·8	2′–15″	1′–52″	1′–32″
2·4	0′–40″	0′–34″	0′–32″	2·9	1′–58″	1′–39″	1′–21″
2·5	0′–33″	0′–28″	0′–25″	3·0	1′–45″	1′–27″	1′–13″

TABLE V

$I(A_3A_4)(+ve)$, $II(D)(-ve)$

D. in c.c.	t_{35}	t_{40}	t_{45}	D in c.c.	t_{35}	t_{40}	t_{45}
3·0	2′–35″	2′–18″	2′–4″	4·1	2′–45″	2′–27″	2′–15″
3·1	2′–7″	1′–52″	1′–40″	4·2	2′–7″	1′–48″	1′–42″
3·2	1′–49″	1′–33″	1′–21″	4·3	1′–31″	1′–24″	1′–21″
3·3	1′–22″	1′–11″	1′–4″	4·4	1′–13″	1′–5″	1′–0″
3·4	1′–4″	0′–59″	0′–53″	4·5	0′–56″	0′–49″	0′–44″
3·5	0′–52″	0′–44″	0′–44″	4·6	0′–41″	0′–39″	0′–36″

TABLE VI

$I(B)(+ve)$, $II(G)(-ve)$

G in c.c.	t_{35}	t_{40}	t_{45}
2·0	3′–19″	2′–56″	2′–46″
2·1	2′–50″	2′–38″	2′–28″
2·2	2′–29″	2′–16″	2′–4″
2·3	2′–2″	1′–50″	1′–29″
2·4	1′–42″	1′–29″	1′–19″
2·5	1′–20″	1′–15″	1′–3″

TABLE VII

$I(B_1B_2)(+ve)$, $II(G)(-ve)$

G in c.c.	t_{35}	t_{40}	t_{45}	G in c.c.	t_{35}	t_{40}	t_{45}
2·3	2′–25″	2′–12″	2′–5″	2·5	2′–54″	2′–43″	2′–0″
2·4	1′–54″	1′–50″	1′–45″	2·6	2′–16″	1′–48″	1′–38″
2·5	1′–43″	1′–36″	1′–33″	2·7	1′–43″	1′–34″	1′–13″
2·6	1′–30″	1′–26″	1′–20″	2·8	1′–16″	0′–49″	1′–1″
2·7	1′–16″	1′–11″	1′–5″	2·9	0′–59″	0′–41″	0′–40″
2·8	1′–5″	1′–2″	1′–1″	3·0	0′–49″	..	0′–38″

TABLE VIII

$I(B_3B_4)(+ve)$, $II(G)(-ve)$

G in c.c.	t_{35}	t_{40}	t_{45}	G in c.c.	t_{35}	t_{40}	t_{45}
2·8	2′–5″	1′–59″	1′–53″	3·0	2′–20″	2′–13″	2′–5″
2·9	1′–35″	1′–30″	1′–27″	3·1	2′–8″	2′–2″	1′–53
3·0	1′–78″	1′–13″	1′–9″	3·2	1′–55″	1′–49″	1′–40″
3·1	1′–3″	1′–0″	0′–56″	3·3	1′–43″	1′–38″	1′–34″
3·2	0′–47″	0′–46″	0′–43″	3·4	1′–34″	1′–29″	1′–24″
3·3	0′–38″	0′–35″	0′–34″	3·5	1′–25″	1′–21″	1′–20″

TABLE IX

$I(C)(+ ve)$, $II(E)(- ve)$

E in c.c.	t_{35}	t_{40}	t_{45}
2·5	3′–26″	3 –12″	2′–59″
2·6	3′–4″	2′–52″	2′–42″
2·7	2′–48″	2 –38″	2′–27″
2·8	2′–32″	2′–20″	2′–12″
2·9	2′–12″	2′–2″	1′–54″
3·0	1′–42″	1′–41″	1′–23″

TABLE X

$I(C_1C_2)(+ ve)$, $II(E)(- ve)$

E in c.c.	t_{35}	t_{40}	t_{45}	E in c.c.	t_{35}	t_{40}	t_{45}
2·8	3′–51″	3′–35″	3′–20″	2·7	3′–8″	2′–54″	2′–38″
2·9	3′–33″	3′–18″	3′–2″	2·8	2′–45″	2′–36″	2′–12″
3·0	3′–16″	3′–2″	2′–44″	2·9	2′–18″	2′–11″	2′–5″
3·1	2′–56″	2′–46″	2′–34″	3·0	2′–2″	1′–55″	1′–50″
3·2	2′–45″	2′–37″	2′–18″	3·1	1′–41″	1′–37″	1′–13″
3·3	2′–30″	2′–20″	2′–20″	3·2	1′–16″	1′–9″	0′–47″

TABLE XI

$I(C_3C_4)(+ ve)$, $II(E)(- ve)$

E in c.c.	t_{35}	t_{40}	t_{45}	E in c.c.	t_{35}	t_{40}	t_{45}
2·5	3′–25″	3′–7″	2′–46″	2·8	4′–5″	3′–44″	3′–27″
2·6	3′–2″	2′–47″	2′–28″	2·9	3′–47″	3′–29″	3′–11″
2·7	2′–42″	2′–29″	2′–12″	3·0	3′–18″	3′–5″	2′–46″
2·8	2′–20″	2′–10″	1′–53″	3·1	2′–58″	2′–46″	2′–30″
2·9	1′–58″	1′–49″	1′–32″	3·2	2′–37″	2′–28″	2′–17″
3·0	1′–20″	1′–14″	1′–2″	3·3	2′–25″	2′–22″	2′–18″

TABLE XII

$I(H)(-ve)$, $II(F)(+ve)$

F in c.c.	t_{35}	t_{40}	t_{45}
3·3	6′–14″	6′–3″	5′–50″
3·4	4′–49″	4′–37″	4′–24″
3·5	3′–55″	3′–44″	3′–29″
3·6	2′–12″	1′–59″	1′–45″
3·7	0′–59″	0′–55″	0′–49″
3·8	0′–34″	0′–30″	0′–23″

TABLE XIII

$I(H_1H_2)(-ve)$, $II(F)(+ve)$

F in c.c.	t_{35}	t_{40}	t_{45}	F in c.c.	t_{35}	t_{40}	t_{45}
3·4	6′–10″	5′–54″	5′–40″	3·5	6′–2″	5′–50″	5′–35″
3·5	4′–44″	4′–31″	4′–16″	3·6	5′–21″	5′–3″	4′–50″
3·6	4′–12″	3′–58″	3′–44″	3·7	4′–37″	4′–21″	4′–5″
3·7	3′–27″	3′–12″	2′–58″	3·8	3′–42″	3′–25″	3′–12″
3·8	2′–36″	2′–20″	2′–14″	3·9	2′–49″	2–33″	2′–29″
3·9	1′–50″	1′–41″	1′–36″	4·0	2′–12″	2′–3″	1′–53″

TABLE XIV

$I(H_3H_4)(-ve)$, $II(F)(+ve)$

F in c.c.	t_{35}	t_{40}	t_{45}	F in c.c.	t_{35}	t_{40}	t_{45}
3·6	6′–17″	5′–51″	5′–38″	3·7	5′–48″	5′–25″	5′–14″
3·7	5′–16″	4′–53″	4′–36″	3·8	5′–8″	4′–42″	4′–29″
3·8	4′–24″	4′–1″	3′–46″	3·9	4′–20″	3′–38″	3′–43″
3·9	3′–36″	3′–14″	2′–59″	4·0	3′–48″	3′–24″	3′–20″
4·0	2′–31″	2′–4″	1′–52″	4·1	2′–52″	2′–30″	2′–16″
4·1	1′–58″	1′–28″	1′–20″	4·2	2′–3″	1 –50″	1′–28″

Discussion of Results

(*a*) *Effect of volumes of sols.*—It will be seen from the above tables that the time of setting of gels obtained by the mutual interaction of oppositely charged sols decreases as increasing amounts of sol II are added to the same amount of the sol I. The decrease is rapid for the first few additions but slows down when larger amounts are added. The values of the logarithm of the different volumes (*a*) in c.c. of sol II added to sol I were plotted against the logarithms of the times of setting at 35°, 40° and 45°, and in all cases the plotted points were found to lie either on single straight lines or two intersecting straight lines. The tangents of the inclinations of the lines are negative, showing thereby that the relation $t = Ra^{-m}$ is obeyed in all cases. The values of m and log R, or of m_1 and m_2, and log R_1 and log R_2, in cases where the plotted points lie on two intersecting straight lines, were read from the graphs and the applicability of the above relation was confirmed.

(*b*) *Effect of temperature.*—It will be observed that, in all cases, the time of setting of the same gel-forming mixture decreases as the temperature is increased.

Hurd and Letteron[6] have found that the time of setting (t) of silicic acid gels at several absolute temperatures (T) follows the relation $\frac{d \ln t}{d T} = \frac{Q}{RT^2}$, where Q is the heat of activation of the formation of these gels. They have calculated the values of Q by multiplying the slopes of the straight lines obtained by plotting log t against $\frac{1}{T}$ by 2·3 R. Prasad and Desai[7] have found that the aforesaid relation also applies to the gels studies by them, and have calculated the heat of activation of the formation of these gels.

The values of log t for the same gel-forming mixtures were plotted against $\frac{1}{T}$ and with few exceptions the curves obtained were found to be a set of parallel straight lines. The values of Q were calculated from the slopes of these straight lines and their mean values are given in Table XV.

It was found that several values of Q do not differ from the mean by more than three per cent. in most cases. The obedience of the relation $\frac{d \ln t}{dT} = \frac{Q}{RT^2}$ by gels formed either by metathetical reaction or by the addition of electrolytes to sols, or by mutual gelation, shows that the three methods of the formation of gels are similar.

TABLE XV

Sols	Q	Sols	Q	Sols	Q	Sols	Q
A, D ..	1787	B, G .	2929	C, E ..	2825	H, F ..	1607
A_1, D ..	6642	B_1, G ..	3447	C_1, E ..	3073	H_1, F ..	1478
A_2, D ..	7270	B_2, G ..	6598	C_2, E ..	3727	H_2, F ..	1925
A_3, D ..	5246	B_3, G ..	1636	C_3, E ..	5020	H_3, F ..	2337
A_4, D ..	3849	B_4, G ..	2327	C_4, E ..	3413	H_4, F ..	2539

(*c*) *Effect of dialysis.*—The volumes of the sols of antimony sulphide, silicic acid and manganese dioxide required to form gels with the same volume of aluminium hydroxide sol dialysed to different extent, which set in the same time at the same temperature were determined and are given in Table XVI. Table XVII brings out the same effect in the case of gels obtained by mixing the same volume of nickel hydroxide sol, dialysed to different extent with the silicic acid sol.

TABLE XVI

Days of dialysis of sol A or B or C (+ ve)	Time of setting = 1 minute						Time of setting = 2 minutes		
	c.c. of D (−ve) required for setting with A at			c.c. of G (−ve) required for setting with B at			c.c. of E (−ve) required for setting with C at		
	35°	40°	45°	35°	40°	45°	35°	40°	45°
0 day ..	1·86	1·84	1·78	2·63	2·61	2·51	3·25	2·91	2·85
1 day ..	2·26	2·18	2·11	2·87	2·83	2·81	3·52	3·45	3·37
2 days ..	3·42	3·20	3·17	2·89	2·84	2·75	3·02	2·98	2·91
3 days ..	3·43	3·38	3·34	2·15	3·09	3·06	2·90	2·83	2·77
4 days ..	4·46	4·43	4·39	3·82	3·76	3·71	3·51	3·45	3·36

It will be observed from Table XVI that the greater the period of dialysis of the aluminium hydroxide sol, the larger is the volume of the oppositely charged sol of antimony sulphide and silicic acid required to cause gelation. Table I shows that the cataphoretic speed of the aluminium hydroxide sol increases as it is dialysed for longer period. If the cataphoretic velocity is assumed to be proportional to the density of the electric charge on the colloid

particles of the sol, the data given in the above table support the view that the mutual coagulation of oppositely charged sols, used in these two cases, which precedes gelation, is brought about mostly by the neutralisation of opposite electric charges. The mutual gelation of aluminium hydroxide and manganese dioxide sols show no regularity in this respect.

The results given in Table XVII show that greater the period of dialysis of the nickel hydroxide sol, larger is the volume of the silicic acid

TABLE XVII

Days of dialysis of sol H (−ve)	Time of setting = 2 minutes		
	c.c. of F (+ ve) required for setting with H at		
	35°	40°	45°
0 day ..	3·61	3·60	3·57
1 day ..	3·88	3·85	3·83
2 days ..	4·05	4·01	3·98
3 days ..	4·10	4·02	3·98
4 days ..	4·25	4·18	4·15

sol required to cause gelation in the same time (2 minutes). The cataphoretic speed of the nickel hydroxide sol increases for the first two days of dialysis and then regularly decreases during the subsequent two days (*cf.* Table I). Hence it appears probable that in this case, besides the neutralisation of charges, factors such as the mutual adsorption of colloidal particles, or the interaction between stabilising ions or the excess of free electrolytes in the two sols, also play some part in bringing about the mutual coagulation of sols.

SUMMARY

Gels have been obtained by mixing (i) the positively charged aluminium hydroxide sol (dialysed and undialysed) with negatively charged sols of antimony sulphide, silicic acid and manganese dioxide and (ii) the negatively charged nickel hydroxide sol dialysed to different extent with the positively charged sol of silicic acid.

2. The time of setting (t) of these gels decreases as increasing volumes (a) of a sol are added to the same amount of the oppositely charged

sol. The experimental results show that the relation $t = Ra^{-m}$ is obeyed in most cases.

3. The effect of temperature on the time of setting of these gels shows that Hurd and Letteron's relation $\frac{d \ln t}{d T} = \frac{Q}{RT^2}$ is obeyed in most cases. This indicates that the method of formation of these gels is similar to those of the other gels.

4. The study of the cataphoretic speed and the effect of dialysis on the time of setting of the gels support the view that the mutual coagulation of oppositely charged sols of aluminium hydroxide and (i) antimony sulphide and (ii) silicic acid is brought about mostly by the neutralisation of the opposite electric charges. The other gels studied in this paper do not support this view, probably because other factors also play some part in bringing about mutual coagulation.

References

1. Prasad and Mehta .. *Curr. Sci.*, 1943, **12**, 19.
2. ——— .. *J. Indian Chem. Soc.*, 1943, **22**, 167.
3. Prakash .. *Ibid.*, 1932, **9**, 193.
4. Prasad and Mehta .. *Proc. Nat. Acad. Sci.*, 1943, **13**, 78.
5. Miss Nathan .. *J. Indian Chem. Soc.*, 1943, **20**, 159.
6. Hurd and Letteron .. *J. Phys. Chem.*, 1932, **36**, 604, 2194.
7. Prasad and Desai .. *J. Indian Chem. Soc.*, 1939, **16**, 117.

KINETIC STUDIES IN ESTER HYDROLYSIS

Part III. Acid Hydrolysis of Ethyl Acetate in Mixed Solvents*

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Introduction

In Part II[2] of these studies, it was noticed that the rate of the reaction under investigation showed interesting variations in aqueous glycerol media when the solvent composition was progressively changed from 20% water to 20% glycerol. The present communication deals with a part of a systematic investigation of the nature of solvent effect in acid catalysed and alkaline hydrolysis of esters. The reaction rate has been determined in various dioxane-water and acetone-water mixtures.

Results and Discussion

The results presented in Tables I and II give the bimolecular rate constants and dielectric constants for the various media.

Table I

Velocity constants in dioxan-water mixtures

Composition Vol. % dioxan	Temperature °C.					
	35		45		55	
	Dielectric constant	$k \times 10^5$	Dielectric constant	$k \times 10^5$	Dielectric constant	$k \times 10^5$
0	74·93	28·06	71·49	63·39	68·24	137·5
10	66·13	26·25	63·35	62·81	59·89	134·4
20	57·32	25·82	55·31	59·96	51·70	128·7
40	40·67	21·63	38·48	48·56	36·40	106·8
60	24·82	16·14	23·44	37·20	22·14	82·08
80	10·34	10·96	9·81	27·84	9·31	61·03
90	5·40	11·47	5·20	28·98	5·01	63·30

* The material presented here is part of a thesis of P.M.N., accepted for M.Sc. Degree of Madras University.

TABLE II

Velocity constants in acetone-water mixtures

Composition Vol. % Acetone	Temperature °C.					
	35		45		55	
	Dielectric constant	$k \times 10^5$	Dielectric constant	$k \times 10^5$	Dielectric constant	$k \times 10^5$
0	74·93	28·06	71·49	63·39	68·24	137·50
10	70·63	25·87	67·41	59·21	(64·2)	123·50
20	66·17	23·31	63·14	54·03	(59·3)	110·10
40	56·29	18·17	53·73	40·19	(51·3)	83·71
60	44·99	13·67	42·93	28·76	(41·3)	65·21
80	32·12	9·365	30·62	22·62	(29·0)	49·73
90	25·22	9·649	24·07	24·46	(23·02)	53·46

The dielectric constant values in Tables I and II have been obtained by interpolation using data taken from Akerlof.[1] Values within brackets are computed from the values at lower temperature.

Since it has been well established by Harned and Ross[4] that the first order rate constant is proportional to the catalyst concentration even for media containing extremely high proportions of dioxane, the measurements made are under strictly comparable conditions. Figs. 1 and 2 show the variation of reaction rate with composition of the medium. As can be readily seen from the curves, while in general a lower dielectric constant is associated with a reduced reaction rate, this behaviour does not persist right through and the rate constant passes through a minimum in region of 80% organic solvent. Also, the values obtained make it evident that the two series of solvents have marked specific influence on the reaction rate. Thus, at 35° C. while a change in dielectric constant from 74·93 to 10·34 depresses the value of $k \times 10^5$ from 28·06 to 10·96, in dioxane-water systems, a much smaller change, namely from 74·93 to 32·12 is sufficient to bring about a greater drop (to 9·365) in rate constant in acetone-water systems. The behaviour is the same for higher temperatures. The reaction velocity is, therefore, found to be far more sensitive to changes in dielectric constant in acetone-water mixtures than in mixtures of dioxane and water. The significance of the trend of velocity constants with changing composition of the medium is more fully considered in a separate communication.

FIG. 1. Velocity-composition curves for Acetone-water mixtures.
Curve no. I II III
Temp. 35° C. 45° C. 50° C.

FIG. 2. Velocity-composition curves for Dioxane-water mixtures.
Curve no. I II III
Temp. 35° C. 45° C. 55° C.

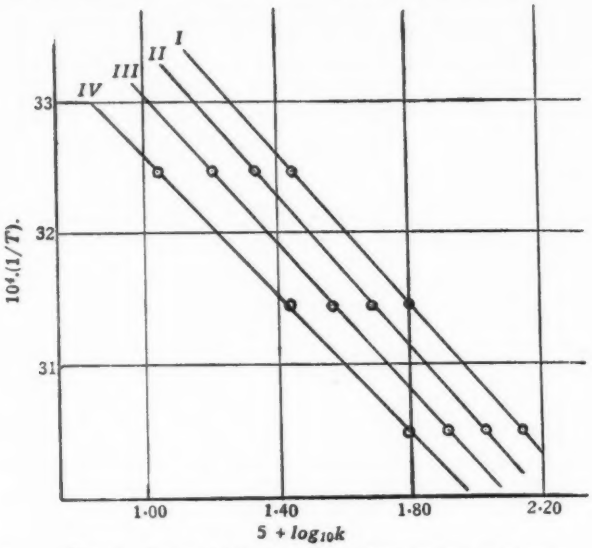

FIG. 3. $Log_{10}k$–1/T curves for Dioxane-water mixtures.

Curve no.	I	II	III	IV
Vol.% of Dioxane	0	40	60	80

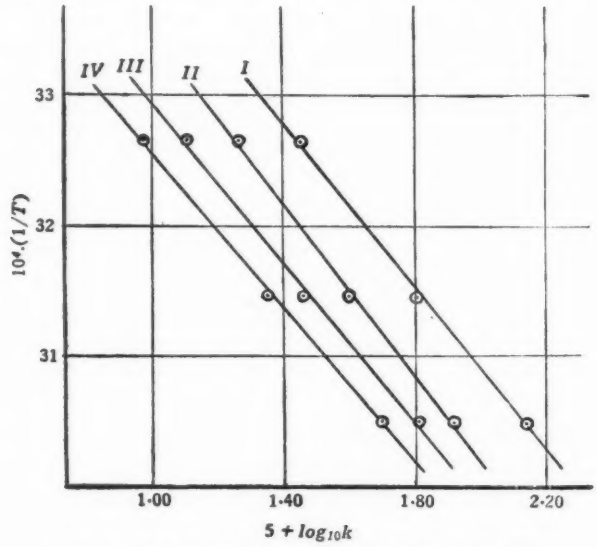

FIG. 4. $Log_{10}k$–1/T curves for Acetone-water mixtures.

Curve no.	I	II	III	IV
Vol.% of Acetone	0	40	60	80

A remarkable feature of the reaction is the strict linearity observed in the log $k - 1/T$ curves (Figs. 3 and 4) for all the solvent compositions and it is interesting here to recall the objections raised by Svirbely and Warner[6] against the conventional method of evaluating activation energies in reactions that are affected by dielectric constant of the solvent. The observed behaviour proves that there is no change in the energy of activation within the temperature range studied and that the correction factor in the expression for iso-dielectric activation energy

$$E_D = E_{app.} + R\left(\frac{\partial lnk}{\partial D}\right)_T \frac{dD}{d(1/T)}$$

is small in comparison with $E_{app.}$ (apparent, *i.e.*, experimental activation energy).

The experimental activation energies and frequency factors are given in Table III.

TABLE III

Solvent composition % of organic solvent by volume	Acetone-water		Dioxan-water	
	Energy of activation in kilocalories per mole	Log of frequency factor	Energy of activation in kilocalories per mole	Log of frequency factor
0	16·000	7·77	16·000	7·77
10	15·700	7·55	16·400	8·05
20	15·600	7·43	16·100	7·86
40	15·300	7·14	16·000	7·71
60	16·400	7·77	16·300	7·78
80	16·800	7·87	17·200	8·23
90	17·200	8·18	17·200	8·27

While the activation energy in acetone-water mixtures shows a position of minimum at about 40% acetone and then progressively rises with increasing proportion of acetone, dioxane-water mixtures show only smaller changes with a possible maximum in the 10% region, minimum in the 40% region and reaches possibly a stationary value after 80% dioxan. However, the variations are too small to admit of any rigid conclusions being drawn from them. In the case of dioxane-water mixtures, this behaviour corroborates the observations of Harned and Ross[4] with methyl acetate that activation energies are not appreciably sensitive to changes in solvent composition and that changes in the values of the frequency factor are

primarily responsible for changes in reaction rate. It should also be mentioned here that the observed trends clearly show that as higher proportions of the organic solvents are used, one has to reckon with Van der Waals forces or a possible change of catalyst or both. Discussion on this aspect has to be deferred until velocity constants for alkaline hydrolysis in these solvents have also been considered.

Experimental

Purification of materials.—Ethyl acetate was purified by the usual method to free it from acid. It was then over calcium chloride for three days and distilled, large head and tail fractions being rejected. B.P. 77·1°/C. 757·6 mm.

1 : 4-Dioxan was purified by the method of Eigenberger.[3] It was refluxed with dilute HCl (100 c.c. of 1 N HCl for every litre of dioxane) for about eight hours to hydrolyse any acetal present and the acetaldehyde formed was removed in a rapid current of air. It was then dried over sticks of pure potassium hydroxide for 48 hours and distilled. The distillate was further dried over analar sodium for three days and finally redistilled over the same. The middle fraction was collected for use. B.P. 100·5°–101° C./754·35 mm.

Acetone was treated with potassium permanganate[5] to free it from easily oxidisable impurities, and left for a week. The manganese dioxide formed was filtered off and the filtrate distilled. The distillate was dried over pure anhydrous potassium carbonate and redistilled. Large head and tail fractions were rejected and the middle fraction coming over between 56·1° and 56·3° C. (under 756·4 mm. pressure) was collected.

The water used was twice distilled with potassium permanganate in a Pyrex all-glass distillation unit, only the middle fractions being used.

Velocity Measurements.—The reactions were carried out in an electrically operated water thermostat which maintained temperature constant within 0·015° C.

N/10 ester solutions were prepared by weighing the necessary amount of ester into a 100 ml. standard flask and adding the appropriate volume of acetone or dioxane from standard pipettes and water enough to bring the level a little below the neck. The flask was then allowed to stand with occasional shaking for about an hour for attainment of room temperature and was then filled up to the mark with water. (For lower percentages of organic solvent, there was very little heat evolved on mixing.) The concentration of each ester solution was determined by complete alkaline hydrolysis in sealed bulbs and back titration of the excess of alkali using bromo thymol blue as indicator,

An aqueous solution of analar HCl (Merck) of strength about 0·625 N was prepared and standardised gravimetrically. The standardisation was checked up with sodium carbonate standard. The required amount of this solution to make 100 c.c. of N/10 solution was pipetted out into a 100 c.c. flask and the preparation of the solution proceeded with as before. The strengths of the acid solutions were determined by titrations just before use.

5 c.c. portions of acid and ester solutions were mixed in bulbs (of 11 to 13 c.c. capacity) at the temperature of a mixture of ice and salt. The bulbs were sealed off and immersed in the thermostat, the time of immersion being taken as zero time. They were withdrawn at suitable intervals and chilled in a freezing mixture of ice and salt. The seals were then broken at the top and the contents of the bulbs poured into 20 c.c. of ice-water (previously boiled and cooled to expel carbon dioxide) in each case and bulbs rinsed carefully with ice-water. The total volume of water used was kept approximately constant at 60 c.c. The chilled mixture was then titrated against standard barium hydroxide (N/40), bromo thymol blue being used as indicator.

Plots of $\log_{10}(a - x)$ against t (where a is the initial concentration and x the fraction of hydrolysed at time t) gave very good straight lines (Fig. 5)

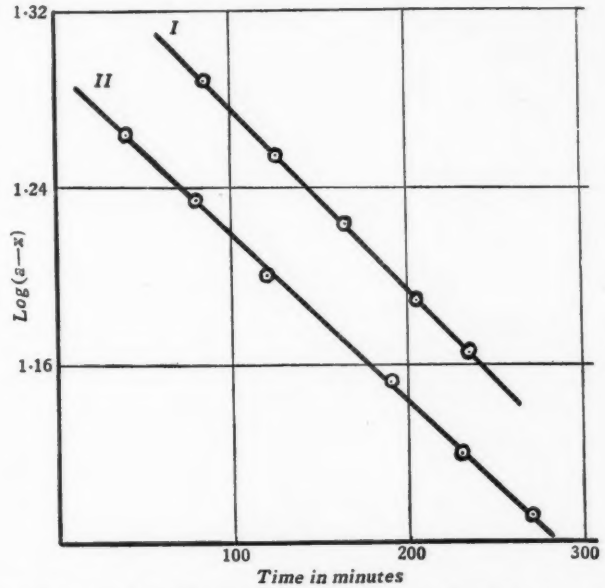

FIG. 5. Plop of log (a–x) against time for acid hydrolysis at 55° C.
No. 1 80% Dioxane. No. 2 60% Acetone.

indicating that the reaction was unimolecular and that there was no drift in the velocity constants within the limit to which the reaction was followed. The slope,

$$\frac{1}{t_2 - t_1} \log_{10} \frac{a - x_1}{a - x_2}$$

of each line was read for different intervals and the average value was used for calculation of the velocity constant.

$$\left(k\,[H^+] = k' = \frac{2 \cdot 303}{t_2 - t_1} \log_{10} \frac{a - x_1}{a - x_2}\right)$$

Typical experimental runs are presented in Tables IV and V.

All the *k*-values were corrected for solvent expansion. The densities for different percentages of organic solvents at the particular temperatures

TABLE IV

Acid hydrolysis of ethyl acetate in acetone-water mixtures at 35° C.

Volume % Acetone	Strength of Hydrolysing Acid	Titre for 5 ml. of acid solution	Baryta equivalent to 5 ml. ester solution						
0	0·0489 N	19·05	20·01	Time in minutes	100·0	200·0	324·0	473·0	573·0	..
				Titre of 10 ml reaction mixture V_t	20·50	21·90	22·40	25·10	26·15	..
10	0·0491 N	20·45	21·35	t	100·0	200·0	300·0	400·0	500·0	700·0
				V_t	21·90	23·40	24·70	25·95	27·10	29·05
20	0·0491 N	20·45	21·65	t	100·0	200·0	300·0	400·0	500·0	600·0
				V_t	21·90	23·25	24·45	25·70	26·70	27·80
40	0·0492 N	20·50	22·00	t	100·0	200·0	300·0	400·0	500·0	600·0
				V_t	21·55	22·65	23·70	24·65	25·62	26·55
60	0·0491 N	21·50	23·77	t	100·0	200·0	300·0	400·0	500·0	601·0
				V_t	22·40	23·25	24·05	24·70	25·55	26·25
80	0·0492 N	21·50	24·05	t	100·0	200·0	300·0	425·0	500·0	600·0
				V_t	22·00	22·60	23·30	24·00	24·45	25·00
90	0·0440 N	18·45	22·60	t	125·0	300·0	415·0	500·0	..	..
				V_t	19·20	20·00	20·60	21·05	..	..

TABLE V

Acid hydrolysis of ethyl acetate in dioxan-water mixtures at 35° C.

Volume % Dioxan	Strength of hdrolysing acid	Titre for 5 ml. of acid	Baryta equivalent to 5 ml. of ester							
0	0·0489 N	19·05	20·01	Time in minutes t	100·0	200·0	324·0	473·0	573·0	..
				Titre of 10 ml. reaction mixture V_t	20·50	21·90	22·40	25·10	26·15	..
10	0·0489 N	19·05	20·00	t	106·1	161·6	256·6	325·0	412·4	473·4
				V_t	20·60	21·40	22·70	23·50	24·50	25·13
20	0·0488 N	19·00	20·30	t	128·8	199·9	305·8	395·9	492·9	624·5
				V_t	20·85	21·85	23·20	24·23	25·25	27·70
40	0·0487 N	20·80	22·65	t	113·2	199·8	370·7	468·3	671·3	..
				V_t	22·43	23·60	25·60	26·65	28·70	..
60	0·0488 N	21·20	22·50	t	122·5	247·5	404·1	604·0	661·0	..
				V_t	22·00	23·30	24·60	26·30	26·70	..
80	0·0488 N	20·75	23·98	t	90·0	180·0	270·0	480·0	580·0	660·0
				V_t	21·38	22·05	22·65	24·10	24·83	25·25
90	0·0607 N	25·75	23·00	t	120·0	240·0	370·0	480·0	601·0	720·0
				V_t	26·68	27·90	28·86	29·70	30·65	31·55

were obtained by interpolation using the data given in Landolt and Bornstein's "Physkalisch Chemische Tabellen" (p. 459) in the case of acetone-water mixtures, and those given by F. Hovorka, R. A. Schæfer and D. Dreisbach[7] in the case of dioxane-water mixtures.

We thank the Chemical Society, London, for a grant and one of us (P. M. N.) has to thank the Madras University for a Studentship that enabled him to take up this investigation.

SUMMARY

The kinetics of the hydrolysis of ethyl acetate in acetone-water and dioxane-water systems are reported. The rate constant passes through a minimum when the concentration of the organic solvent in the medium is in the neighbourhood of 80%. The temperature variation conforms strictly to the Arrhenius equation even for media containing extremely high

proportions of organic solvent. Even though the activation energy is affected by changes in solvent composition, the variations are not sufficiently marked for an analysis. The frequency factor has got a tendency to follow the trend of activation energies.

References

1. Akerlof .. *J. Am. Chem. Soc.*, 1932, 4129 ; 1936, **58**, 1241.
2. Anantakrishnan and Krishnamoorthi, S. .. *Proc. Ind. Acad. Sci.*, 1941, **14 A**, 279.
3. Eigenberger .. *J. Prakt. Chem.*, 1931, **130**, 75.
4. Harned and Ross .. *J. Am. Chem. Soc.*, 1941, **63**, 1993.
5. Norris and Psentiss .. *J. Chem. Soc.*, 1928, 129.
6. Svirbely and Warner .. *J. Am. Chem. Soc.*, 1935, **57**, 1883.
7. Hovorka, Schæfer and Dreisbach .. *Ibid.*, 1936, **58**, 2264.

HIGH ALTITUDE INTENSITY OF PENETRATING COSMIC RAYS AT POONA 9° N. (mag.)

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(Communicated by Prof. H. J. Bhabha, F.R.S.)

As part of the programme of the Tata Institute of Fundamental Research initiated by Dr. H. J. Bhabha in 1945 to measure and study the variation of the intensity of the different components of cosmic radiation with altitude at different latitudes throughout India, the authors have conducted a number of balloon flight experiments at Poona, 9° N. (mag.), during the months of April and May 1949. The measurements were made with quadruple-coincidence counter telescopes, without lead absorber and also with 10 cm. of lead between the counters. The geometry of the telescopes was the same as that used in the previous flights[1] with the sole difference that the diameter of the counters was now 4·2 cm. instead of 3·5 cm. The extreme counters of all the (identical) quadruple-coincidence telescopes defined a cone making angles of 7·5° and 25° with the vertical. The temperature inside the gondola which contained the apparatus was maintained above + 10° C., even at the highest altitudes reached, by using the "greenhouse effect". Quadruple-coincidences, together with the atmospheric pressure and temperature inside the gondola, were transmitted continuously over a single ultra-high-frequency radio carrier to the ground receiving apparatus, which recorded the information automatically on a moving paper tape. In the previous experiments[1] two separate channels were used, one for the cosmic-ray counts and another for the meteorological elements.

All the four flights made with 10 cm. of lead absorber were successful in giving reliable intensity data up to altitudes of 60,000 feet, corresponding to a pressure of 100 millibars. A typical curve showing intensity *vs.* pressure in millibars for a telescope with 10 cm. of lead absorber is given in the accompanying figure, with the root-mean-square deviations marked on the points. It will be seen that there is some indication of a maximum in the neighbourhood of 250 mb., followed by a minimum and a subsequent rise beyond 150 mb. Although this feature appears on three of the curves its reality must be considered doubtful, since the scatter of the points is somewhat large owing to the relatively low counting rate. The results are consistent

with a monotonic increase in the intensity of the hard component to the lowest pressures reached by the apparatus.

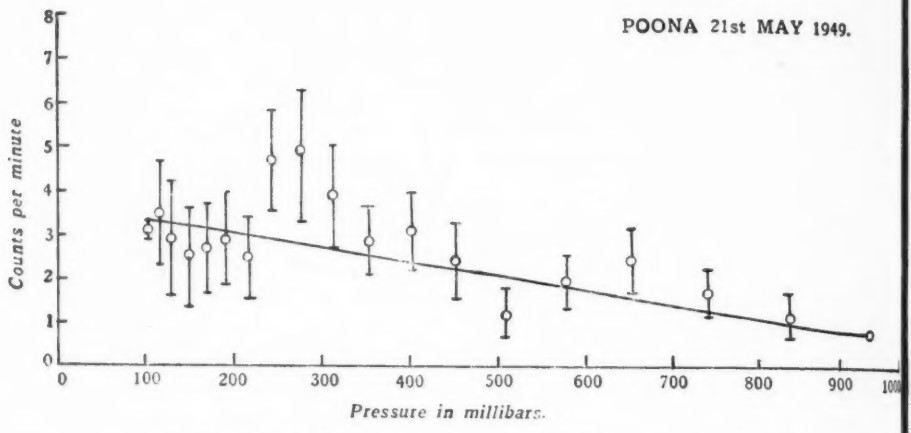

FIG. 1. Vertical Intensity of Cosmic radiation penetrating 10 cm. of Lead.

The vertical intensity of the penetrating component of cosmic-rays has been measured by several groups of workers, as for example Schein, Wollan and Groetzinger,[2] Bhabha, Aiya, Hotcko and Saxena,[3] Schein, Jesse and Wollan,[4] Gill, Schein and Yngve,[5] Pomerantz,[6] and J. R. Winckler, W. G. Stroud and J. Schenck,[7] using lead absorbers varying in thickness from 2 to 30 cm. Most of these workers have found that the hard component intensity continues to increase monotonically to the lowest pressures their apparatus could reach, except Dymond[8] who has reported that the vertical hard component under 10 cm. of lead at 59° N. geomagnetic latitude passes through a maximum at 107 millibars.

Similar flights from Bangalore 3° N. (mag.) have been planned in the near future. A fuller account of these experiments will be published later.

It is a great pleasure to express our gratitude to the India Meteorological Department for the facilities provided for the flights and especially to Mr. S. P. Venkiteswaran and his staff of the Instrument Section of the Poona Meteorological Office for their co-operation and help.

We are greatly indebted to Prof. H. J. Bhabha for his guidance of this work.

Summary

High-altitude balloon flight experiments were conducted at Poona 9° N. (mag.) to measure cosmic-ray intensity with quadruple-coincidence counter telescopes with 10 cm. of lead between the counters, using the radiosonde technique. Heights of 60,000 ft. (100 mb.) were reached. It is concluded that the intensity of cosmic radiation penetrating 10 cm. of lead absorber increases monotonically with decreasing atmospheric pressure.

References

1. G. S. Gokhale, A. S. Rao, and R. P. Thatte .. *Proc. Ind. Acad. Sci.*, **1949, 30**, 184.
2. M. Schein, E. O. Wollan and G. Groetzinger .. *Phys. Rev.*, 1940, **58**, 1027.
3. H. J. Bhabha, S. V. C. Aiya, H. E. Hoteko and R. C. Saxena .. *Ibid.*, 1945, **68**, 147.
4. M. Schein, W. P. Jesse and E. O. Wollan .. *Ibid.*, 1941, **59**, 615.
5. P. S. Gill, M. Schein and V. Yngve .. *Ibid.*, 1947, **72**, 733.
6. M. A. Pomerantz .. *Ibid.*, 1949, **75**, 69.
7. J. R. Winckler, W. G. Stroud and J. Schenck .. *Ibid.*, 1948, **74**, 837.
8. E. G. Dymond .. *Nature*, 1939, **144**, 782.

COSMIC RAY INTENSITY MEASUREMENTS AT BANGALORE 3° N. (mag.)

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Received May 29, 1950
(Communicated by Prof. H. J. Bhabha, F.R.S.)

§ 1. Introduction

In continuation of the programme of the Tata Institute of Fundamental Research initiated by Dr. H. J. Bhabha in 1945, to measure and study the variation of the intensity of the different components of cosmic radiation with altitude at different latitudes throughout India,[1,2,3] the authors have conducted a number of balloon flight experiments at Bangalore 3° N. (mag.) during the months of February and March, 1950. Seven successful flights were made and some of them reached altitudes as high as 27·5 km. corresponding to a pressure of 30 mb. Quadruple-coincidence telescopes were used: (1) with single-counter trays and 10 cm. of lead absorber; (2) with double-counter trays and 10 cm. of lead absorber; (3) with double-counter trays without absorber. The intensity of the vertical penetrating component was measured by (1) and (2), and the total vertical intensity by (3). The geometry of the telescopes is given in Figs. 1 (*a*), (*b*), (*c*). Figs. 1 (*a*) and (*b*) show the end views of the single and double counter tray quadruple-coincidence telescopes respectively and Fig. 1 (*c*) represents the side view of the telescopes which is the same for both. The shaded areas indicate the position of the lead absorbers.

The technique of telemetering the signals from the air-borne apparatus to the ground receiving station is the same as that used in the previous flights,[1] except that a single ultra-high-frequency radio carrier was used to transmit the quadruple-coincidences, atmospheric pressure, and the temperature inside the gondola. The pressure and temperature signals were transmitted as pulses with a width of the order of 0·5 sec. whereas the cosmic-ray quadruple-coincidence pulses were about 1/5th the width of the former. There was thus no possibility of confusing the different pulses. The pulses were recorded automatically on a moving paper tape at the ground receiving station. The temperature inside the gondola which contained the apparatus was maintained above + 10° C., even at the highest altitudes reached, by using the "greenhouse effect".

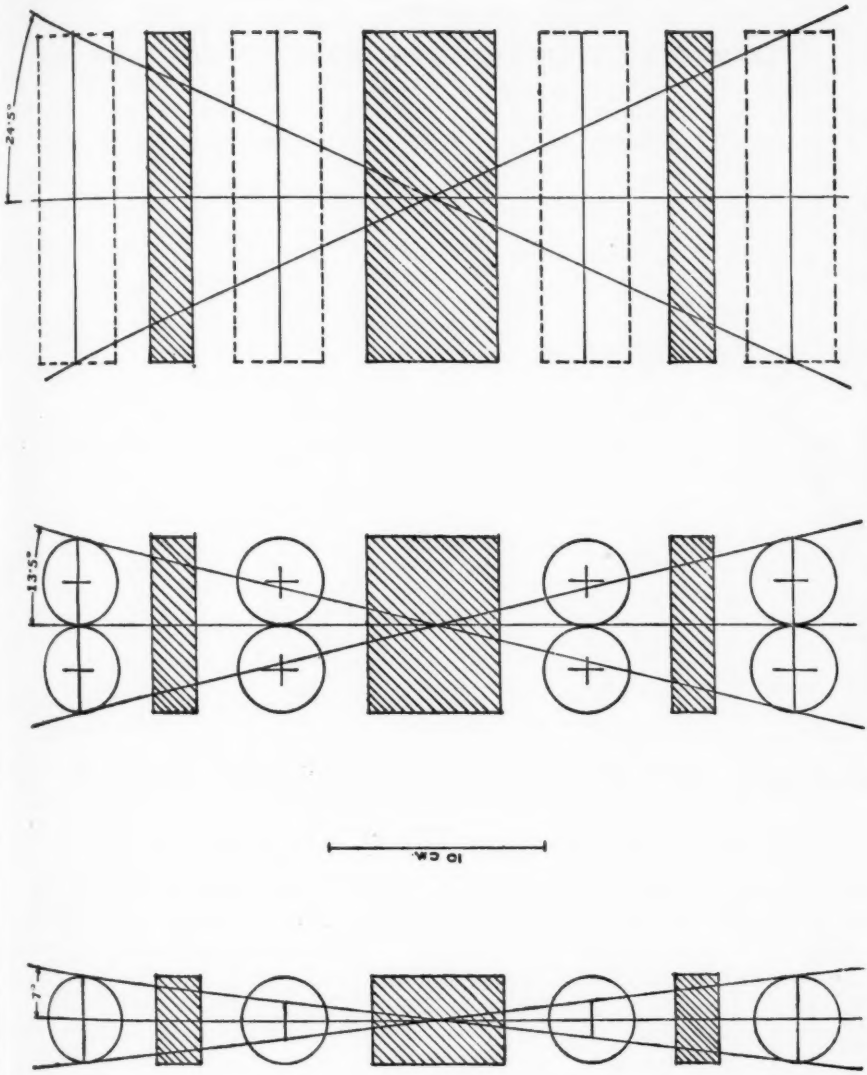

FIG. 1. Geometry of the Telescopes (*a*) with single counters (*b*) with double counters (*c*) side view.

§ 2. Measurement of the Total Vertical Intensity

The total vertical intensity of cosmic radiation as a function of altitude was measured up to a height of 27·5 km., corresponding to a pressure of 30 mb., using a quadruple-coincidence telescope with double-counter trays. The results thus obtained are given in Fig. 2. The root-mean-square devia-

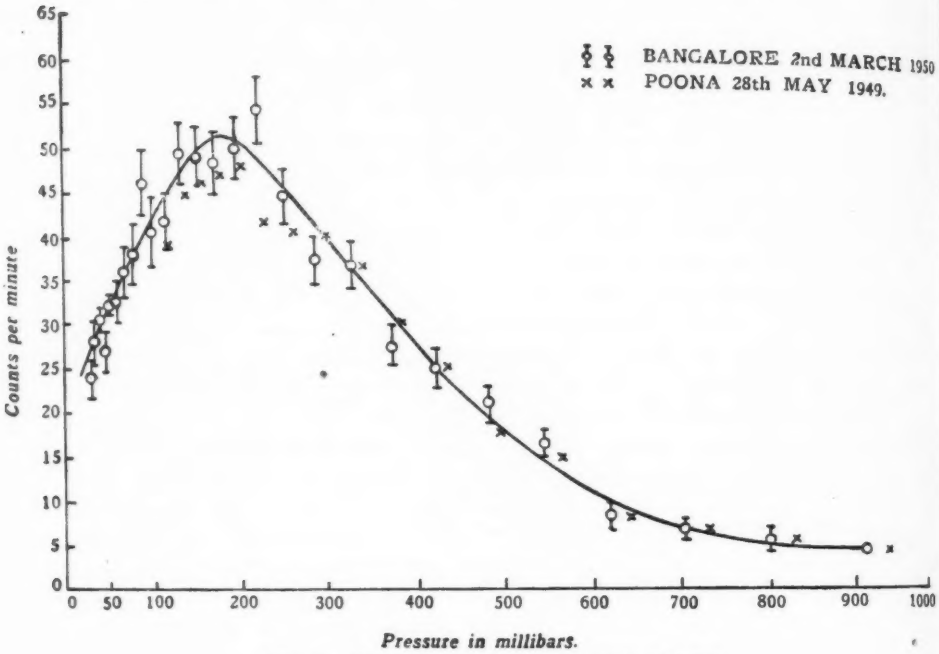

Fig. 2. Total vertical intensity of cosmic radiation.

tion is given for each point. The total vertical intensity obtained at Poona in our previous flights with a similar telescope is also indicated on the same curve. The two sets of observations agree very well with each other, showing that there is no detectable difference in the total vertical intensity between Bangalore 3° N. (mag.) and Poona 9° N. (mag.), which also confirms Neher and Pickering's observations.[4]

§ 3. Measurements of the Vertical Penetrating Component

(*a*) *Single-counter trays.*—The vertical intensity of cosmic radiation penetrating 10 cm. of lead was obtained in four flights with identical quadruple-concidence telescopes with single-counter trays. The semi-angles of the telescopes were $7° \times 24·5°$. Two typical curves showing

intensity *vs.* pressure in millibars are given in Fig. 3 with the root-mean-square deviation given for each point. Although the scatter of the points

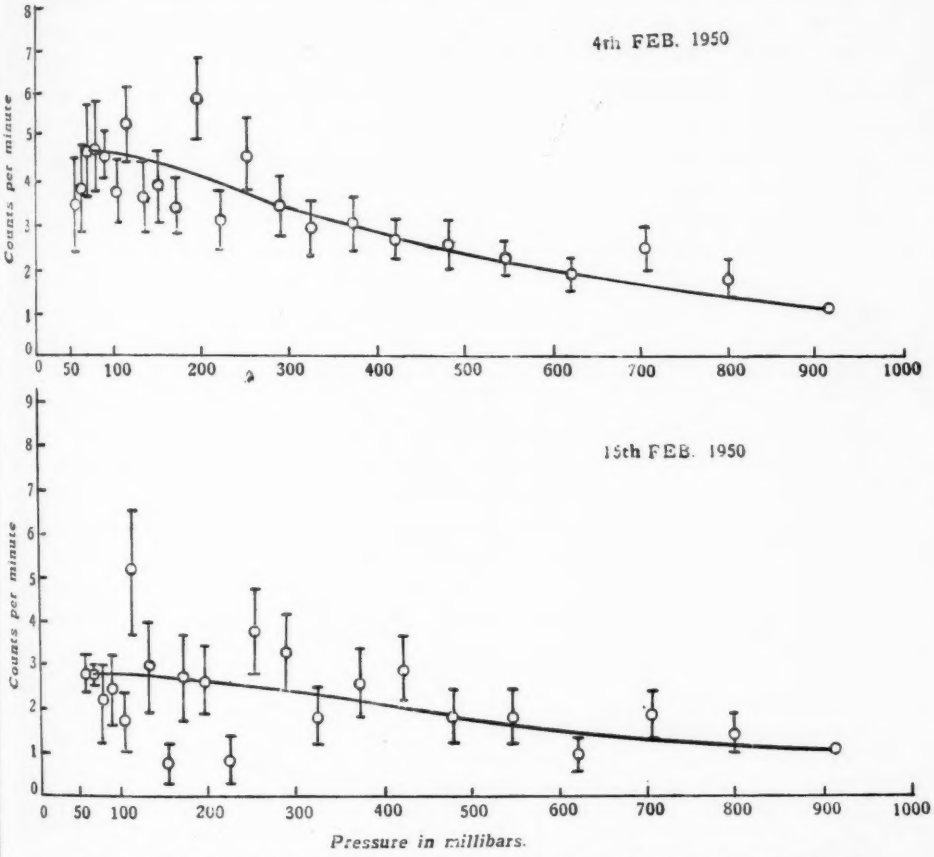
4th FEB. 1950
15th FEB. 1950
Counts per minute
Counts per minute
0 50 100 200 300 400 500 600 700 800 900 1000
Pressure in millibars.

FIG. 3. Vertical intensity of cosmic radiation penetrating 10 cm. of lead (Quadruple coincidences with single-counter trays).

is rather large owing to the relatively low counting rate, all the curves show qualitative agreement in their general features, namely that the intensity increases monotonically with decreasing pressure up to the lowest pressures reached by the apparatus. However, they differ quantitatively in that the ratios of the intensity at 100 mb. level to that at ground level in the four flights are 2·7, 4·0, 2·4 and 4·2 respectively even though all four telescopes were standardised and showed rates on the ground which were 1·05, 1·04, 1·07 and 1·09 respectively.

(*b*) *Double-counter trays.*—In order to reduce statistical fluctuations in the counting rates, telescopes with two counters in parallel in each tray, with 10 cm. of lead absorber, were sent up in two flights to measure the intensity of the penetrating component. The semi-angle of the telescope was $14° \times 24 \cdot 5°$. The intensity *vs.* pressure curves of the two flights are given in Fig. 4. These curves are similar to those obtained with single-counter

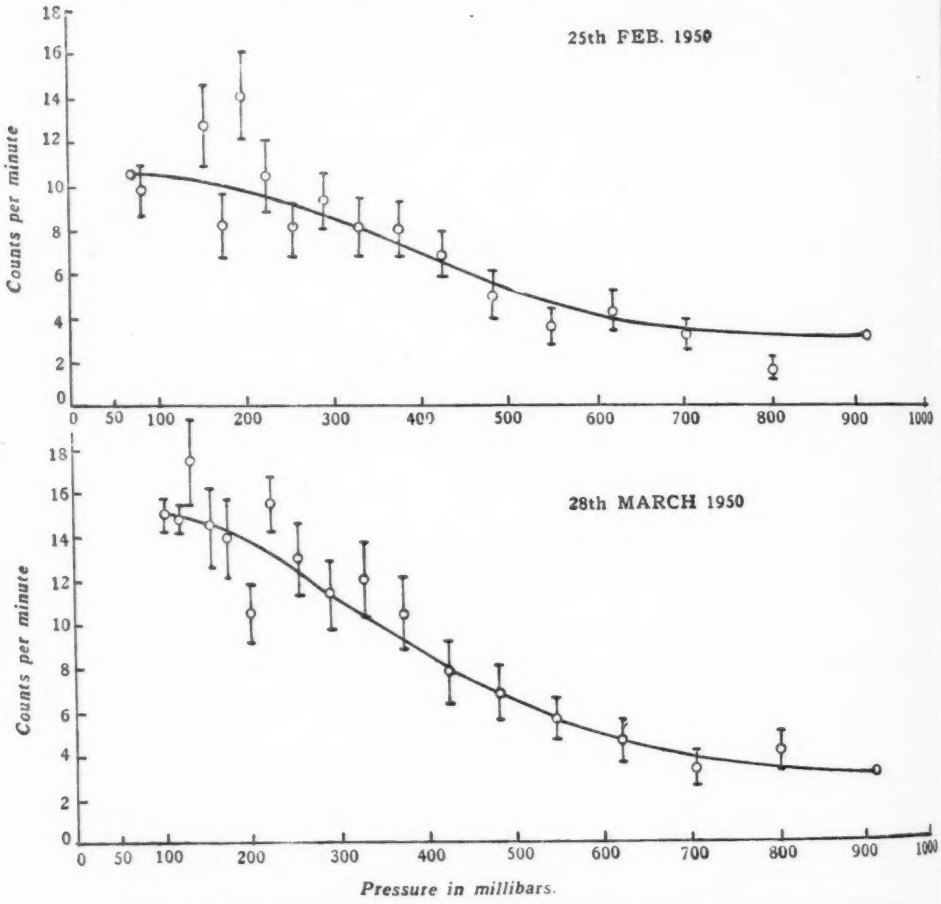

FIG. 4. Vertical intensity of cosmic radiation penetrating 10 cm. of lead (Quadruple coincidences with double-counter trays).

trays, with the same lead absorber. In both of these double-counter tray flights, the intensity increases gradually with decrease of pressure up to the

minimum pressures reached by the apparatus, but again the two curves do not agree quantitatively. The ratios of the intensity at 100 mb. level to that at ground level are 4·6 and 3·4 respectively.

§ 4. Discussion

Every telescope was individually tested on the ground for about 12 hours before it was sent up, to make sure that it was dependable. The average ground counting rates of the four telescopes with single-counter trays with 10 cm. of lead absorber, were all between 1·04 and 1·09 showing that the geometry and efficiency must have been closely similar in all cases. The two telescopes with double-counter trays were also closely alike in geometry and efficiency, and gave ground counting rates of 3·20 and 3·28. In spite of this, the rate of increase of intensity with altitude varies greatly from flight to flight. In view of the care taken to ensure that the telescopes were behaving as nearly as possible identically, and the nearly constant temperature maintained in the gondola we find it difficult to ascribe the variations in the rate of increase of intensity with height solely to instrumental causes. These differences are large, and appear even in the flights made with double-counter trays, which are more reliable statistically. It has been suggested to us by Dr. H. J. Bhabha that these variations may be caused by variations in the temperatures of the atmosphere at very great heights. For a change in the extension of the uppermost layers of the atmosphere would considerably alter the intensity of the observed penetrating component, if this were produced by the primary cosmic rays indirectly through a very short-lived intermediate link. Further experiments will be conducted in the near future to see if these differences in the rate of increase are real and significant. It is also proposed to study the temperature variations of the upper atmosphere from day to day to see whether they show any correlation with the variations in the intensity of the penetrating component.

The authors acknowledge indebtedness to the Government of Mysore for the facilities provided for the flights and especially to Mr. T. V. Ramachandra Ayer, Meteorologist to the Government of Mysore, Bangalore, and to his staff, for their co-operation and help. It is a great pleasure to thank the India Meteorological Department for the supply of hydrogen, and Mr. S. P. Venkiteswaran, Meteorologist, Poona Meteorological Department, for the supply of F. type meteorographs.

We wish to express our gratitude to Prof. H. J. Bhabha for his invaluable guidance and encouragement throughout the progress of this work.

§ 5. Summary

A number of balloon flight experiments were conducted at Bangalore 3° N. (mag.) to measure and study the variation of the different components of cosmic radiation with altitude. Total vertical intensity was obtained with quadruple-coincidence telescopes with double-counter trays up to an altitude of 27·5 km. The vertical intensity of cosmic radiation penetrating 10 cm. of lead was measured by quadruple-coincidence telescopes with single-counter trays and with double-counter trays. The intensity of the penetrating component increases monotonically with altitude in all the flights, but the ratio of the intensity at 100 mb. level to that at ground level differs by as much as 50% from flight to flight, although the ground intensity agrees in all cases to within 3%, and the measurements were made with standard telescopes.

§ 6. References

1. R. P. Thatte — *Journal of Scientific and Industrial Research*, 1949, **8**, 259.
2. G. S. Gokhale, A. S. Rao and R. P. Thatte — *Proc. Ind. Acad. Sci.*, 1949, **30**, 184.
3. K. S. Chandrasekharan, G. S. Gokhale and A. S. Rao — *Proc. Ind. Acad. Sci.*, 1950, **32**, 95.
4. H. V. Neher and W. H. Pickering — *Phys. Rev.*, 1942, **61**, 407.

RAMAN SPECTRUM OF ANHYDRITE

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Received June 26, 1950

1. Introduction

The Raman spectrum of anhydrite ($CaSO_4$) was first investigated by Rasetti (1932) using the λ 2536·5 mercury resonance radiation as exciter. He recorded ten Raman lines including four low frequency or lattice lines. A year later, Nisi (1933) photographed the Raman spectrum of anhydrite using the λ 4358 excitation and identified eleven frequency shifts of which nine were due to the internal oscillations of the sulphate ion. The only other experimental work on the Raman effect in anhydrite is that of Lucienne Couture (1948). She investigated the effect of crystal orientation on the intensities of eight of the nine Raman lines due to the sulphate ion. She did not study the lattice spectrum. Thus, it is clear that though the spectrum of the internal oscillations of anhydrite has been recorded in full, the lattice spectrum of anhydrite is far from being properly studied. It should contain many more Raman lines than have been recorded hitherto. This would be obvious when one examines the group theoretical analysis of the vibration spectrum of anhydrite lattice given later in the paper. A re-investigation of the Raman spectrum of anhydrite was therefore called for. This has been carried out by the authors using the well-known ultra-violet excitation and the results are presented here.

2. Experimental Details and Results

The specimen of anhydrite used in the present investigation was obtained from the Geological Survey of India. The authors are indebted to Dr. W. D. West, Director of the Geological Survey of India, for the loan of the specimen. It had the following dimensions: 15×9×7 mm., the edges being parallel to *a*, *b* and *c* axes respectively.

An enlarged photograph of the Raman spectrum of anhydrite taken with the large E 1 quartz spectrograph using a slit-width of 0·04 mm. and an exposure of 6 days is reproduced in Fig. 1. The corresponding microphotometer record is reproduced in Fig. 2. The recorded spectrum exhibits seventeen Raman lines, the frequency shifts of which are tabulated below along with those reported by the earlier investigators. Four new Raman lines have been recorded in the low frequency shift region.

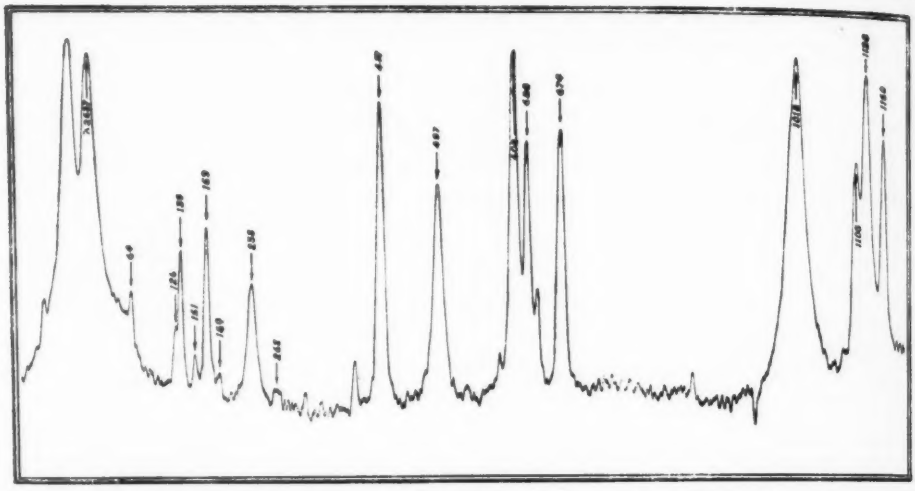

FIG. 2. Microphotometer record of the Raman spectrum of anhydrite taken with E_1 quartz spectrograph.

TABLE I

Sl. No.	Authors	Couture	Rasetti	Nisi
1	62 (4)			
2	126 (3)		122	
3	135 (6)		133	
4	151 (2)			
5	169 (8)		169	166
6	184 (1)			
7	233 (6)		233	227
8	262 (1)			
9	415·5(8)	416		416
10	497 (10)	495	499	499
11	608 (8)	604		609
12	628 (8)	626		628
13	674 (2)	672	676	673
14	1018 (20)	1015	1019	1016
15	1108 (6)	1107	1113	1104
16	1128 (16)	1125	1129	1128
17	1160 (10)	1157	1160	1159

The relative intensities of the lines (figures given in brackets) are for the case when the light was incident normal to the *c* face and the scattered light was taken perpendicular to the *a* face. The intense Raman lines with frequency shifts 417, 608 and 1018 cm.$^{-1}$ fall very close to the three mercury lines λ 2563·9, λ 2576·3 and λ 2603·2 respectively. But their existence has

been verified independently by their appearance on the anti-Stokes side of the spectrum (see Fig. 3).

3. Effect of Crystal Orientation

Three spectrograms corresponding to three different orientations of the anhydrite crystal with reference to the directions of incidence and observation were taken using the medium quartz spectrograph. They are reproduced in Fig. 3. I and S represent directions of incidence and scattering respectively. For example, the spectrum marked *ba* was taken with the incident beam parallel to *b* axis. The depth of illumination for orientation *cb* was only two-thirds of that for the other two orientations. The frequency shifts of those Raman lines which exhibit marked variations in intensity with orientation are indicated in the figure. The lines with frequency shifts 233, 417, 674, 1018 and 1128 cm.$^{-1}$ have minimum intensity for the orientation *cb*.

4. Discussion

Anhydrite belongs to the orthorhombic class with the space group V_h^{17}. A group theoretical analysis of the vibration spectrum of anhydrite was first carried out by Bhagavantam (1938) on the basis that the unit cell contained four molecules of $CaSO_4$. But according to Wasastjerna (1926) the smallest cell should contain only two molecules of $CaSO_4$. It was on this basis that Lucienne Couture (1948) made a theoretical study of the internal frequencies of the Raman spectrum of anhydrite in order to explain the observed variation in intensity of the SO_4 frequencies with orientation. The complete character table for the anhydrite structure is given in Table II. n_i, T, T′, R and n_i', represent the total number of oscillations, translations, translatory type of external oscillations, rotatory type of external oscillations and the internal oscillations respectively. The Table given here is slightly different from that given by Bhagavantam (1938) as the former is based on the fact that the unit cell contains only two molecules of $CaSO_4$. The notations A_{2g}, B_{1g}, and B_{2g} given in Table II correspond respectively to the notations B_{2g}, B_{3g} and B_{1g} adopted by Lucienne Couture.

Internal frequencies of the SO_4 ion.—The analysis shows that there are 18 internal oscillations of which nine are active in Raman effect. They arise as a consequence of the removal of degeneracies of three of the four distinct modes of oscillation appropriate to the free SO_4 ion. The nine Raman lines due to internal oscillations observed in the spectrum of anhydrite have been classified by Couture as follows: 415·5 (B_{1g}), 497 (A_{1g}), 608 (A_{2g}), 628 (B_{2g}), 674 (A_{1g}), 1018 (A_{1g}), 1108 (A_{2g}), 1128 (A_{1g}) and 1160 (B_{2g}). As is to be expected, the lines 497, 674, 1018 and 1128 cm.$^{-1}$

TABLE II

Anhydrite

V_h^{17}	E	C′	$C_2^{(S)}$	$C_2^{(S)}$	i	$\sigma_h^{(g)}$	σ_v	σ_v'	n_i	T	T′	R′	n_i'	Raman	Infra-red
A_{1g} ..	1	1	1	1	1	1	1	1	6	0	2	0	4	P	F
A_{2g} ..	1	−1	1	−1	1	−1	1	−1	5	0	2	1	2	P	F
B_{1g} ..	1	1	−1	−1	1	1	−1	−1	2	0	0	1	1	P	F
B_{2g} ..	1	−1	−1	1	1	−1	−1	1	5	0	2	1	2	P	F
A_{1u} ..	1	1	1	1	−1	−1	−1	−1	2	0	0	1	1	F	F
A_{2u} ..	1	−1	1	−1	−1	1	−1	1	5	1	1	1	2	F	P
B_{1u} ..	1	1	−1	−1	−1	−1	1	1	6	1	1	0	4	F	P
B_{2u} ..	1	−1	−1	1	−1	1	1	−1	5	1	1	1	2	F	P
$U_R(S)$ ..	4	4	0	0	0	0	4	4							
$U_R(S-\nu)$ ..	2	2	0	0	0	0	2	2							
$h\rho\chi_\rho'(T)$	3	−1	−1	−1	−3	1	1	1							
$h\rho\chi_\rho'(T')$	9	−3	1	1	3	−1	3	3							
$h\rho\chi_\rho'(R')$	6	−2	0	0	0	0	−2	−2							

coming under A_1 (symmetric) class exhibit marked variations in intensity with orientation (see Fig. 3).

Lattice Oscillations.—Of the fifteen external oscillations, 6 of the translatory type and 3 of the rotatory type should be active in Raman effect. Actually, 8 lattice lines with the frequency shifts 62, 126, 135, 151, 169, 184, 233 and 262 cm.$^{-1}$ have been recorded. The ninth oscillation may have been too weak to be recorded with the small specimen of anhydrite used in the present investigation. Of the six Raman-active translatory oscillations, two come under the symmetric (A_{1g}) class. They may be expected to exhibit marked variations in intensity with orientation. The two lattice lines which behave in this manner are 126 and 233. (See Fig. 3) They should therefore be identified as the translatory oscillations coming under the symmetric class. Besides these, there are three sharp lines with frequency shifts 62, 135 and 169 cm.$^{-1}$ which are fairly intense (see Fig. 1). They may be assigned as the three rotatory oscillations which are allowed in the Raman effect. Further detailed classification and identification of the modes

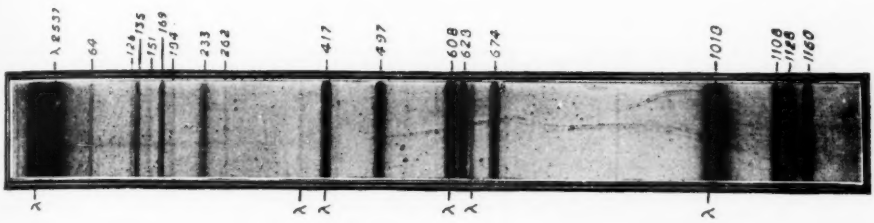

FIG. 1. Raman spectrum of anhydrite taken with E 1 quartz spectrograph

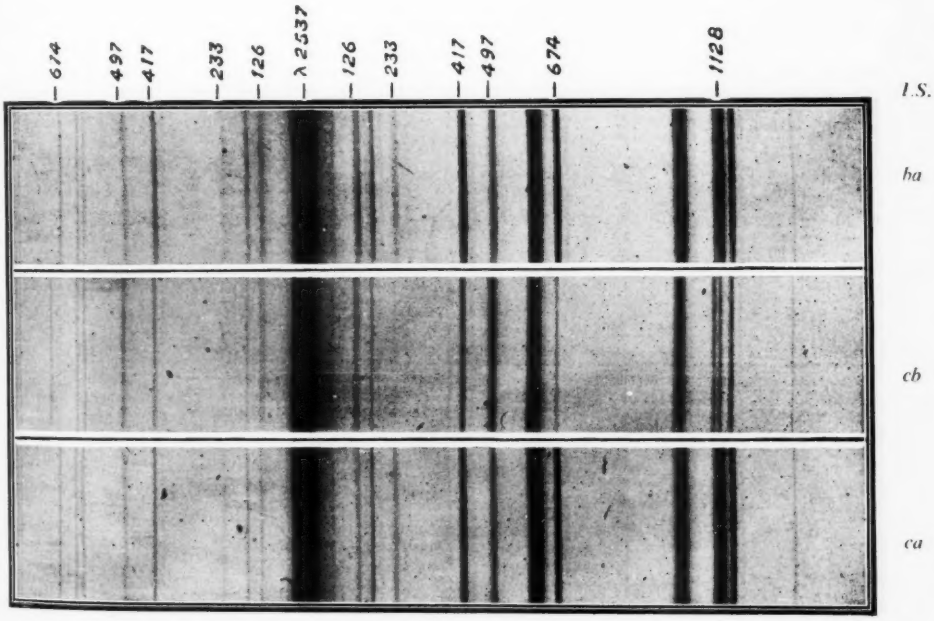

FIG. 3. Raman spectra of anhydrite in different orientations

could be made only after obtaining data concerning the polarisation characteristics of the lattice lines.

5. Summary

Using $\lambda 2536{\cdot}5$ mercury resonance radiation as exciter, the Raman spectrum of a single crystal of anhydrite has been investigated for three different orientations. Besides the nine Raman lines due to the sulphate ion, the recorded spectrum exhibits eight of the nine lattice lines to be expected theoretically. Their frequency shifts are 62, 126, 135, 151, 169, 184, 233 and 262 cm.$^{-1}$ From the observed variations in intensity with orientation, tentative assignments have been given to the lattice lines.

References

1. Bhagavantam, S. .. *Proc. Ind. Acad. Sci.*, 1938, **8 A**, 345.
2. Couture, L. .. *Journ. de Physique*, 1948, **9**, 84.
3. Nisi, H. .. *Proc. Phys. Math. Soc. Japan*, 1933, **15**, 463.
4. Rasetti, F. .. *Nuovo Cimento*, 1932, **9**, 72.
5. Wasastjerna .. *Phil. Mag.*, 1926, **2**, 992.

NUCLEAR OXIDATION IN FLAVONES AND RELATED COMPOUNDS

Part XXX. A New Synthesis of Asarone

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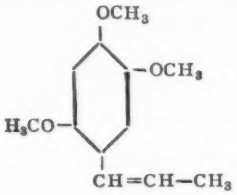
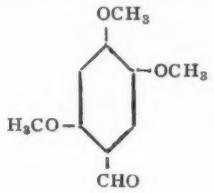
Asarone (I) is an important isomer of elemicin and occurs in the ethereal oils of *Asarum arifolium*, *Asarum europeum* and *Acorus calamus*. Its constitution was established and its first synthesis was effected by Gattermann and Eggers.[1] They heated for this purpose asarylic aldehyde (II) with propionic anhydride and sodium propionate in a sealed tube for 7 hours



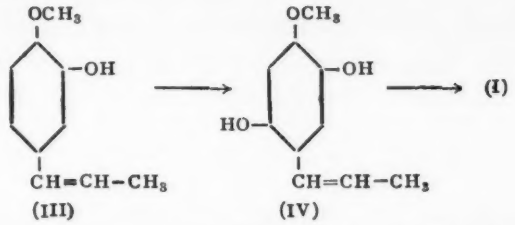
(I)



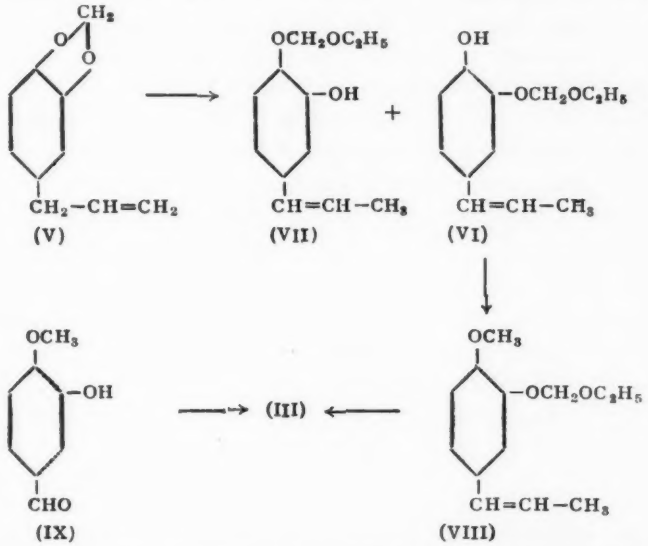
(II)

at 150°. More recently Bert[2] has effected the synthesis starting from the trimethyl ether of hydroxy-hydroquinone and 1 : 3-dichloro-propylene.

In Part XXIV[3] of this series the idea was discussed that among allyl and propenyl benzene compounds present in essential oils, the catechol derivatives represent more fundamental stages in biogenesis, and the synthesis of elemicin and myristicin (pyrogallol derivatives) was carried out conveniently starting from eugenol and using the two stage process of ortho oxidation. Asarone has a fully methylated hydroxy-quinol unit and has a propenyl side chain. For its preparation the appropriate catechol derivative would be isochavibetol (III). Though this particular compound does not occur in nature, its isomer chavibetol is found in betel leaves. The isomerisation to isocompounds is fairly facile in this series. It is therefore suggested that asarone (I) is evolved in plants from isochavibetol (III) by a process involving para nuclear oxidation (IV) and methylation. This transformation has now been effected in the laboratory and it represents a new synthesis of asarone. The synthetic compound agrees in its properties and in its derivatives with natural asarone. It may be mentioned here that the method of nuclear oxidation has been successfully applied in our laboratory for the preparation of asaronic acid, aldehyde and related compounds.[7]



Isochavibetol (III) was obtained first by the isomerisation of chavibetol with alcoholic potash.[4] It was also made by the transformation of safrole[5] (V). By the action of ethyl alcoholic potash on safrol (V) a mixture of two phenols, ethoxy isoeugenol (VI) and ethoxy isochavibetol (VII) was obtained. The mixture was separated through the benzoates. The former (VI) was subsequently methylated with dimethyl sulphate and alkali and the product (VIII) hydrolysed with alcoholic hydrochloric acid when isochavibetol (III) was produced. Later it was prepared (10% yield) by



the application of the Grignard reaction using isovanillin (IX) and excess of magnesium ethyl iodide.[6] For our present purpose we have adopted the convenient process in which isovanillin (IX) is condensed with sodium propionate and propionic anhydride. The product is isochavibetol propionate and on hydrolysis yields isochavibetol (III) agreeing in its properties and derivatives with the natural product.

Experimental

Isochavibetol (III):

Isovanillin (2 g.), propionic anhydride (8 c.c.) and freshly fused sodium propionate (2 g.) were heated together in an oil-bath at 140–50° for seven hours. The resulting liquid was then poured into ice water (150 c.c.) and left overnight. A semi-solid mass was thus obtained. It was dissolved in ether, the ether extract shaken well with excess of sodium carbonate solution, washed with water and then distilled to remove the ether. The residue was insoluble in aqueous alkali and should thus be the propionate of isochavibetol. It was refluxed with alcoholic potash for half an hour, the alcohol removed under reduced pressure and the residue treated with dilute hydrochloric acid. The dark reddish brown viscous liquid collecting at the bottom was dissolved in ether and the ether extract washed with water and dried over anhydrous sodium sulphate. On distilling off the ether an oily liquid was left behind which soon solidified to a pale brown solid mass (1 g.). It crystallised from ethyl acetate-benzene mixture to give colourless rectangular rods melting at 95–96°. It had a characteristic odour, gave a yellow solution with aqueous sodium hydroxide and a bluish green colour with alcoholic ferric chloride. (Found: C, 72·9; H, 7·1; $C_{10}H_{12}O_2$ requires C, 73·2; H, 7·3%.) The acetate crystallised from ethyl acetate-petroleum ether mixture as clusters of colourless needles melting at 99–100°.

3 : 6-*Dihydroxy*-4-*methoxy*-1-*propenyl benzene (IV)*:

To a stirred ice-cooled solution of isochavibetol (4 g.) in aqueous sodium hydroxide (3 g. in 60 c.c.) a solution of sodium persulphate (6 g.) in water (60 c.c.) was added drop by drop in the course of one and a half hours. After 24 hours the solution was acidified to congo red when a dark semi-solid containing unchanged isochavibetol separated. This was removed by shaking thrice with ether, 75 c.c. each time (ether solution A). Concentrated hydrochloric acid (25 c.c.) and sodium hydrogen sulphite (0·5 g.) were then added to the aqueous solution which was heated on a boiling water-bath for fifteen minutes and cooled when a dark brown precipitate was obtained. It was filtered, the filtrate saturated with sodium chloride and extracted with ether repeatedly. On evaporating the ether some more of the brown solid was obtained. The total yield was 0·2 g. About half of the isochavibetol could be recovered unchanged from ether solution A. The experiment was repeated a number of times to get material enough for characterisation and for the subsequent methylation experiment.

The dihydroxy compound was crystallised from ethyl acetate to give colourless rectangular prisms melting at 136°. It was soluble in alkali forming

a brownish yellow solution which slowly changed to darker brown. With alcoholic ferric chloride it gave a transient green colour with a tinge of blue changing to brown very quickly. An alcoholic solution of it turned brown in a few minutes on adding an alcoholic solution of *p*-benzoquinone. (Found: C, 66·6; H, 6·7; $C_{10}H_{12}O_3$ requires C, 66·6; H, 6·7%.)

Asarone (*I*):

The above dihydroxy compound (0·5 g.) was methylated by refluxing in anhydrous acetone solution (100 c.c.) with dimethyl sulphate (0·8 c.c.) and anhydrous potassium carbonate (3 g.) for six hours. The solution was filtered and the potassium salts washed with acetone. The solvent was distilled off from the combined filtrate and washings, when an oily liquid was left behind. It was dissolved in ether (50 c.c.) and the ether solution shaken twice with aqueous alkali (20 c.c.), washed with water and dried over anhydrous sodium sulphate. On distilling off the ether, a viscous brown liquid was left behind which soon solidified. It was dissolved in light petroleum and the solution allowed to evaporate gradually. Colourless needles were thus deposited on the sides of the test-tube when the solution was concentrated to half its original volume. The crystals of asarone thus obtained were filtered. The melting point was found to be 62–3°. (Found: C, 69·4; H, 7·8; $C_{12}H_{16}O_3$ requires C, 69·2; H, 7·7%.) The dibromide was prepared by treating the asarone sample in chloroform solution in the cold with excess of bromine. The solvent was then distilled off and the residue crystallised from acetone when it was obtained as colourless plates melting at 86–7° with decomposition.

Summary

Based on considerations of biogenesis asarone is now synthesised from isochavibetol by para nuclear oxidation with alkaline persulphate and subsequent methylation. Isochavibetol needed for this purpose is conveniently prepared by the condensation isovanillin with propionic anhydride and sodium propionate.

References

1. Gattermann and Eggers .. *Ber.*, 1899, **32**, 289.
2. Bert .. *Compt. Rend.*, 1941, **213**, 873.
3. Rao, Seshadri and Thiruvengadam *Proc. Ind. Acad. Sci.*, **A**, 1949, **30**, 114.
4. Bertram and Gildemeister .. *J. Pr. Chem.*, (2), 1889, **39**, 349.
5. Ciamician and Silber .. *Ber.*, 1892, **25**, 1472.
   Pomeranz .. *J. C. S., Abs.*, 1901, 699.
   Hirao .. *Jour. Chem. Soc. Japan*, 1930, **51**, 579.
6. Behal and Tiffeneau .. *Bull. Soc. Chim.*, 1908, (4), **3**, 308.
7. Rajagopalan, *et al.* .. *Proc. Ind. Acad. Sci.*, **A**, 1949, **30**, 265.

MUSTARD OILS AND MUSTARD OIL GLUCOSIDES OCCURRING IN THE SEED KERNELS OF *PUTRANJIVA ROXBURGHII* WALL.

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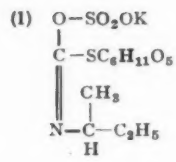
Gambhir and Dutt[1] have reported the presence of phenyl mustard oil (phenyl-*iso*-thiocyanate) in the fatty oil from the seeds of *Putranjiva roxburghii* Wall. (Family Euphorbiaceæ) which the earlier work of Krishna and Puntambekar,[2] had not recorded. To find the possible cause of this discrepancy, therefore, the oil, obtained both by petroleum-ether extraction and by cold hydraulic expression of the putranjiva kernels at different stages of their development, was re-examined. It was discovered that the "mustard" smell was highest in the fatty oil (mustard oil content being 35% of the amount present in the kernels) from the kernels of fully grown but green fruit, medium in those of the ripe fruit, and negligible in those that had fallen on the ground for a long period.[3] It was further observed that in every case when the kernels were extracted with petroleum-ether, they yielded four times as much "mustard" constituent in the fatty oil as that obtained by cold hydraulic expression. From the findings recorded in Table I it is clear that the occurrence of mustard oil along with the fatty oil depends upon the moisture in the kernels. If the kernels are ripe but wet, the mustard oil which is liberated by enzymic hydrolysis of the component glucosides is produced in large quantity, but if the kernels are dry the mustard oil is absent. If, therefore, dry kernels are used, as they usually are, for the extraction of the fatty oil, the mustard oil is missing. This explains the reason for our having missed the mustard oil in our earlier work.[2]

During the course of the present investigation the oil which has been designated as mustard oil turned out to be a mixture of phenyl, *iso*propyl and *sec*-butyl mustard oils. Of these *iso*propyl mustard oil forms the largest part (approx. 70%) and phenyl mustard oil the least (approx. 3%). These are separated through fractional distillation and identified through their thiourea derivatives.

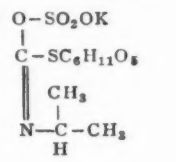
The pulp of the fruit and the leaves were also examined for the possible presence of mustard oils or their glucosides, but none were found. The pulp, however, yielded a large proportion of mannitol and a small amount of amorphous non-sulphur glucoside from which a crystalline aglucon has been isolated and is under further examination.

Out of the three mustard oils found in putranjiva seed kernels, only secondary butyl mustard oil has been recorded in literature[4] to occur in the form of its glucoside, gluco-cochlearin, in the leaves, seeds and flowers of *Cochlearia officinalis* Linn. and in the leaves, stems and roots of *Cardamine amara* Linn. and *C. pratensis* Linn. The glucoside, however, has not been isolated in pure form. The presence of the other two mustard oils, namely, *iso*propyl and phenyl mustard oils, has not so far been reported in any other plant.

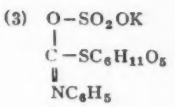
Of the few mustard oil glucosides reported in literature only sinigrin and sinalbin from the seeds of *Brassica* sp. and glucocheirolin from the seeds of *Cheiranthus* sp., all belonging to the Cruciferæ family, have so far been isolated in pure form. The others owing to their hygroscopic nature and to the difficulty involved in their separation from accompanying sugars and glucosides, have been identified through their products of hydrolysis and characteristic reaction products with silver nitrate. To this category belong the following glucosides, namely, gluconasturtiin from the seeds of *Nasturtium officinale* R.Br.; glucotropæolin from the seeds of *Tropæolum majus* Linn. and *Lepidum sativum* Linn. and the abovementioned gluco-cochlearin from the seeds, leaves and flowers of *Colchlearia officinalis* Linn. Purification of these glucosides by means of lead acetate and subsequent deleading with hydrogen sulphide has been found to bring about their decomposition. In the present work also the same difficulty of isolation of the three mustard oil glucosides in pure form was experienced. Thus their fractional crystallization from alcohol and alcohol-ether mixture was not successful, nor was it found possible to free them completely from accompanying reducing compounds. Their presence could be proved directly only by the study of the general properties of the mustard glucosides, namely, enzymic and acid hydrolysis and formation of silver salt, and indirectly by the isolation of individual mustard oils, as described above. The finding of dextrose and potassium acid sulphate among the products of acid hydrolysis of the mixed glucosides completes their characterization and suggests their formulæ. Out of the three glucosides the *sec*-butyl mustard oil glucoside is already known as glucococochlearin[4] and the names for *iso*propyl and phenyl mustard glucosides are now proposed as follows:—



Sec.-butyl mustard oil glucoside or glucocochlearin



*Iso*propyl mustard oil glucoside or glucoputranjivin



Phenyl mustard oil glucoside or glucojiaputin

It is well known that the medicinal properties of the mustard seed (mustard plaster) are due to the action of the mustard oil (allyl *iso*thiocyanate) liberated in the presence of moisture from the glucoside sinigrin contained in them. This mustard oil is stated to be a powerful rubefacient. Diluted either with alcohol or lard it is applied as a counter-irritant to sprains and is used for rheumatism and similar conditions. Morel[5] found that allyl *iso*thiocyanate has marked bacteriostatic powers especially against the tubercle bacillus. The volatile mustard oil has been used as a substitute for mustard plaster; for this purpose one part of it may be mixed with 60 parts alcohol and the mixture sprinkled not too thickly on muslin and covered with waxed paper. It is said to act quickly and effectively. In view of the fact that the stones of the putranjiva fruit in the form of rosaries are hung round the necks of young children to keep them in good health, it may be that the protection against the diseases of childhood is actually given by one or all of these three mustard oils slowly liberated from the glucosides of the seeds in contact with body moisture.

Mustard oils and mustard oil glucosides have been commonly found in plants of the family Cruciferæ, particularly its genus *Brassica*. They have also been reported to occur, although sparingly, in plants of the families Capparidaceæ, Tropæolaceæ, Salvadoraceæ and Resedaceæ. No record, however, exists of their presence in the family Euphorbiaceæ to which *Putranjiva roxburghii* Wall. belongs.

Experimental

(*a*) *Examination of the Fatty Oil for Mustard Oils*

Putranjiva fruits were collected locally in the following manner:— (1) Fully grown, unripe and plucked from trees, (2) ripe and plucked from the trees, and (3) fallen on the ground. After removal of the pulp the stones were crushed and the kernels handpicked. It was noticed that the moist kernels from the fully grown but unripe fruit gave a strong mustard smell, those of the ripe ones gave a mild mustard smell but those from the

fallen fruit (air-dried) gave no smell at all. When, however, the kernels of the fallen fruits were moistened and left for some time the mustard smell developed. In order to prove this in a quantitative way each group (600 g.) of kernels was divided into two equal parts and the fatty oil from the one was obtained by cold expression and from the other by petroleum ether (60-80° C.) extraction and sulphur content (which is really the index of mustard oil present) of each determined by Carius method. The data are recorded in the table below:—

TABLE I

Sample	Condition of fruit	Method of extraction of fatty oil from kernel	Sulphur content of the fatty oil (Carius)
1 (*a*)	Fully grown unripe and plucked from trees	Petroleum-ether (60–80°)	1·05%
1 (*b*)	do ..	Cold hydraulic expression	0·26%
2 (*a*)	Ripe and plucked from trees ..	Petroleum-ether (60 80°)	0·55%
2 (*b*)	do ..	Cold hydraulic expression	0·14%
3 (*a*)	Fallen on ground and air-dried ..	Petroleum-ether (60–80°)	0·05%
3 (*b*)	do ..	Cold hydraulic expression	Traces

The sulphur content of the kernels of the air-dry seeds fallen on the ground was found to be 1·7% (on dry basis). This corresponds to the presence of 10·8% of the mixed mustard glucosides or 2·8% of the mixed mustard oils in the kernels with sulphur content of 15·7% and 26·32% respectively. It was therefore expected that on complete hydrolysis of the mustard glucosides in 100 g. of the dry kernels 2·8 g. of the mixed mustard oils would be liberated and subsequently extracted along with the fatty oil of the kernels by the organic solvent used for the purpose. Theoretically therefore the fatty oil (25% in the dry kernel) thus extracted should have four times the sulphur content, namely, 2·95% of the total quantity of mustard oils completely liberated from 100 g. of dry kernel. Actually however under the comparable natural conditions as recorded in Table I 3 (*a*), for the seeds fallen on ground and air dried the sulphur content of the solvent extracted fatty oil from the kernels has been found to be 0·05% indicating thereby that only 1·7% of the mustard oils present in the kernels is extractable along with the fatty oil by an organic solvent. Compared to these figures the corresponding figures for the sulphur and mustard oil content of the kernels from fully grown unripe fruit plucked

from trees [Table I 1(*a*)] turn out to be 1·05% and 35% respectively. It might be pointed out in this connection that the yield of mustard oil in the kernels by the fermentation method described below is 0·5% and which amounts to 18% of the total mustard oil actually present in them.

(*b*) *Isolation of Mustard Oils from the Wetted Kernels*

In order to obtain the maximum quantity of mustard oils the following procedure was adopted:—

300 g. of the kernels were reduced to a fine paste, with water, and allowed to stand, in a closed vessel, overnight. Strong mustard smell developed. The mass was then steam-distilled, the distillate saturated with common-salt and extracted with sulphuric ether. The ethereal extract was dried over anhydrous sodium sulphate, ether removed and 1·5 g. of a sharp-smelling brownish-yellow mustard oil (yield 0·5%) obtained. Working in lots of 300 g. a total of 40 g. of the mustard oil of the following characteristics was collected from 8 kilos of kernels:—

Specific gravity at 25° C.	1·027
Refractive index at 25° C.	1·5187
Specific rotation $[\alpha]_D^{25°C.}$ (C = 5% in 95% alcohol)	+ 15°

(*c*) *Fractional Distillation of the Mustard Oil*

36 g. of the oil was fractionally distilled in a 50 c.c. Claisen flask at atmospheric pressure and the following fractions were collected:—

TABLE II

Fraction	B.P.(°C.)	Smell	Weight	Sp. G. at 20° C.	$[\alpha]_D^{25°C.}$	Remarks
0	Below 60	..	1·2 g.	..	..	Mostly ether sulphuric
1	135—45	Strong mustard	18 g.	0·9365	+10·9	Boils mostly at 136–38° C.
2	145—55	do	10 g.	0·9697	+26·0	Boils mostly at 153–55° C.
3	155—65	Mustared + Repulsive	1·8 g.	0·9900	..	Slight decomposition
4	Residue	Repulsive	5 g.	1·5102	..	Decomposed material

Fraction 0 had a mixed smell of mustard and sulphuric ether. It consisted mostly of the residual sulphuric ether with which the mustard oils were extracted from the steam distillate and a little mustard oil also distilled along with it. The mixture was treated with 10% ammonia and slowly

evaporated. Crystals of a thiourea were obtained and identified by its melting point and unaltered mixed melting point with *iso*propyl thiourea prepared from fraction 1.

Fraction 1 was refractionated and the major portion boiling at 136–38° C. collected separately. The thiourea derivative of this had the melting point 164–65° C. (found: S, 27·4%; *iso*propyl thiourea $C_4H_{10}N_2S$ requires S, 27·1%). The presence of *iso*propyl mustard oil was confirmed as follows:

A small portion of the refractionated material was hydrolysed by refluxing for three hours with 20% HCl, whereby *iso*propylamine hydrochloride, carbon dioxide and hydrogen sulphide (lead acetate test) were obtained.

$$(CH_3)_2CH - N = C = S + 2H_2O + HCl \rightarrow (CH_3)_2CH - \\ - NH_2HCl + CO_2 + H_2S$$

The hydrolysate was treated with chloroplatinic acid and evaporated to a small volume when beautiful shining small orange flakes of m.p. 228–30° C. crystallised out. Their mixed melting point with pure synthetic *iso*propyl amine chloroplatinate remained unaltered. The optical rotation of the fraction was due to the presence of a small amount of another mustard oil (secondary butyl mustard oil) identified in fraction 2. The fraction is thus mostly *iso*propyl mustard oil with a small quantity of *sec*-butyl mustard oil.

Fraction 2 was refractionated and the major portion boiling at 157–60° C. was collected. The thiourea derivative of this had the m.p. 137–38° C. (found: S, 24° 4%; $C_5H_{12}N_2S$ requires S, 24·2%). The presence of secondary butyl mustard oil was confirmed as follows:—

A small part of the refractionated material was hydrolyzed by refluxing for three hours with 20% HCl, yielding *sec*-butyl amine hydrochloride, carbon dioxide and hydrogen sulphide.

$$CH_3 - CH_2 - \underset{\displaystyle CH_3}{\underset{|}{CH}} - N = C = S + 2H_2O + HCl \rightarrow CH_3 - CH_2 - \underset{\displaystyle CH_3}{\underset{|}{CH}} - \\ - NH_2 \cdot HCl + CO_2 + H_2S$$

The hydrolysate was treated with chloroplatinic acid, and was evaporated to a small volume when golden yellow plates crystallised out, m.p. 208–10° C. Their mixed melting point with pure synthetic *sec*-butyl amine chloroplatinate remained unaltered. The correct sulphur content but lower specific rotation of the thiourea derivative [found $(\alpha)_D^{25°\,C.} + 10$, requires

$[\alpha]_D^{25° C.} + 22·77]$ of the fraction indicates the presence of racemic *sec*-butyl thiourea and consequently of racemic *sec*-butyl mustard oil.

Fraction 3 had a milder smell of mustard as well as a slightly unpleasant smell of sulphur compounds, probably due to some pyrolysis of the mustard oil. On converting a small portion to thiourea, crystals of indefinite melting point, 130–50° C. were obtained. The fraction was, therefore, distilled a couple of times with alcohol to remove any volatile constituents. Both the distillate and the residue were treated with 10% ammonia and evaporated to dryness. The thiourea so formed on crystallisation from water melted at 139–40° C. and 153–54° C. respectively. The melting point of the former and its unchanged mixed melting point with thiourea isolated from fraction 2 established its identity with *sec*-butyl thiourea prepared from fraction 2. The melting point of the latter, its unchanged mixed melting point with phenyl thiourea from synthetic phenyl mustard oil and its sulphur content (found: S, 21·5%; $C_7H_8N_2S$ requires S, 21·0%) established its identity as phenyl thiourea. The fraction is thus a mixture of *sec*-butyl and phenyl mustard oils.

Residue was a thick dark repulsive smelling oil containing sulphur and appeared to be some pyrolytic products of mustard oils. It did not yield any thiourea.

(*d*) *Isolation of the Mustard Oil Glucosides from the Kernels*

300 g. of kernel powder of the air-dried seeds fallen on the ground was first extracted with petroleum ether in a soxhlet to remove the fatty oil, then thrice successively with boiling 90–95% alcohol and the alcohol removed under vacuum. The viscous residue was taken up in cold water and filtered from the waxy precipitate. The filtrate was shaken with a little barium carbonate to remove any free acidic substances, heated to boiling, cooled, filtered again, decolourized with animal charcoal, reduced to a small volume under vacuum and allowed to crystallise. Since crystallisation did not take place in cold from single or mixed solvents its purification was tried by dissolving it thrice successively in 95% alcohol and precipitating it out by addition of ether. Even at this stage the material showed the presence of reducing compounds with Fehling's solution. The product was dried in vacuum at 50° for 4 hours and further left in vacuum for several days. It was a pale-brown, amorphous highly hygroscopic bitter substance and gave a strong test for sulphur. It was soluble in alcohol and water but insoluble in ether, chloroform and benzene. With neutral lead acetate t gave a slight precipitate. With basic lead acetate a thick white precipitate

was formed after addition of ammonia to the mixture. The water solution was dextrorotatory $[\alpha]_D^{25° C.} + 18·51$ (C = 3·46%). With silver nitrate (10%) it gave a thick dark violet precipitate which dissolved in ammonia, a characteristic property shown by all the mustard glucosides so far isolated from natural sources (0·1500 g. of the silver salt gives 0·1080 g. AgCl, theory requires 0·1025 g. AgCl). On slight warming with 10% HCl it was hydrolysed and the characteristic strong smell of mustard oil was produced. Amongst the other products of hydrolysis potassium acid sulphate and dextrose were identified in the following manner:—

Potassium acid sulphate.—The dry kernel powder was first extracted with petroleum ether to remove the fatty oil. It was then wetted with water and left in an incubator overnight at 38°. After a couple of hours the characteristic smell of mustard developed and increased with the length of time. On the following day, *i.e.*, after 20 hours, the mixture was thoroughly extracted with ether to remove the mustard oil that was formed. After two further successive overnight incubation at 38° C. and ether extractions to remove any mustard oil, the residual kernel paste was diluted with water, the mixture filtered and the residue on the filter was further washed a couple of times with water. The total filtrate on decolourisation with animal charcoal and concentration nearly to dryness under vacuum deposited a large amount of heavy gritty white crystals. These were extracted with warm alcohol (95%) twice to remove all the reducing sugars and the crystalline gritty residue recrystallised from water. On analysis it turned out to be potassium acid sulphate.

Dextrose.—The alcoholic extract was reduced to a small volume under vacuum at 70° C. A portion of the residue was taken up in water decolourised and made to 100 c.c. in a volumetric flask. Its specific rotation was found to be $[\alpha]_D^{30° C.} + 48°$ (C = 3·1%). It reduces Fehling's solution (5 c.c. gave 0·3260 g. Cu_2O, calculated for glucose 0·3360 g. Cu_2O). The sugar was identified as dextrose by the formation of phenyl osazone (m.p. 207–08°) with phenyl hydrazine and of saccharid acid by oxidation with nitric acid.

Summary

Besides phenyl mustard oil reported by Gambhir and Dutt two other mustard oils, namely *iso*propyl and *sec*-butyl *iso*-thiocyanates, have been isolated from the steam volatile oil (yield 0·5%) of the wet kernels of *Putranjiva roxburghii* Wall. All the three mustard oils (69% isopropyl, 28% *sec*-butyl and 3% phenyl mustard oils) are derived from glucosides present in the seed kernels and are only liberated from them in the presence of moisture

by enzymic hydrolysis along with dextrose and potassium acid sulphate. Under these moist conditions it is found that as much as 35% of the mustard oils are extracted by petroleum-ether from the kernels along with the fatty oil but only to the extent of 1·7% if the kernels are dry. Fatty oil expressed from dry kernels contain only traces of the mustard oils.

Out of these mustard oils only *sec*-butyl mustard oil has been previously reported to occur in the plants of the Cruciferæ or mustard family but all the three are now found for the first time in a plant of the Euphorbiaceæ family. The characteristic mustard smell of the moist kernels is due to *iso*propyl and *sec*-butyl mustard oils, the principal constituents of the steam volatile oil isolated from them.

While mustard oil glucosides have been isolated in the form of their mixture their individual isolation has not been possible owing to their highly hygroscopic nature and due to the difficulty of obtaining them in the crystalline state.

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References

1. Gambhir and Dutt .. *Indian Soap J.*, 1946, **11 (8)**, 169–71.
2. Krishna and Puntambekar .. *J. Indian Chem. Soc.*, 1931, **8 (6)**, 301–06.
3. Krishna and Puntambekar .. *Indian Soap J.*, 1946, **2**, 23.
4. Klein, G. .. *Handbuch der Pflanzenanalyse*, 1932, **Bd. 3 (2)**, 1094.
5. Morel .. *Compt. Rend. Soc. Biol.*, 1937, **124 (188)**, 749.

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